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BLENDS OF POLYIMIDES WITH POLY(ETHER ETHER KETONE) AND PEEK DERIVATIVES

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by
ROBERT J. KARCHA

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Dedicated to the memory of my uncle and namesake
Robert Glasser,
whose untimely death prevented
the completion of his dissertation.

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ABSTRACT

BLENDS OF POLYIMIDES WITH POLY(ETHER ETHER KETONE)
AND PEEK DERIVATIVES

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The major theme of this dissertation is the study of blends of polyimides with a series of chemically similar polymers, namely poly(ether ether ketone) (PEEK) and three derivatives of PEEK. The synthesis of two new polymers is discussed, as well as the phase behavior of three new completely miscible blends and one partially miscible blend.

Sulfonated and sulfamidated PEEKs have been prepared, based on previously determined methods. The first controlled nitration of PEEK is reported. Spectroscopic characterization was performed to determine the substitution pattern. Thermal analysis was performed to determine the dependence of the glass transition temperature and the degradation behavior on the level of substitution. Room temperature solubility has been examined for the nitrated PEEKs in fourteen common solvents.

Three methods of reduction of the nitrated polymer to the corresponding aminated polymer have been attempted. Infrared

spectroscopy was used to determine the effectiveness of these methods. Thermal properties and solubility of the reduced polymer are compared to those of the parent nitrated PEEK.

Six different binary blands and one ternary blend have been studied to determine miscibility, defined by the existence of a single glass transition temperature. The phase behavior of binary blends of a commercial poly(amide imide) with poly(ether ether ketone), sulfonated PEEK (three degrees of sulfonation), sulfamidated PEEK, nitrated PEEK (three degrees of nitration) and a commercially available poly(ether imide) have been determined, as well as the behavior of the binary poly(ether imide) - sulfonated PEEK blend (three degrees of sulfonation). Chemical modification of PEEK was found to have a critical effect on the miscibility of these blends: unmodified PEEK was found to be completely immiscible with the poly(amide imide), yet each PEEK derivative showed partial or complete miscibility. Spectroscopic investigation of the intermolecular interactions responsible for the phase behavior found strong deviations from Beer's law in the ultraviolet region; this was postulated to result from the formation of electron donor-acceptor complexes between the substituted phenylene rings of the PEEKs and the N-phenylene units of the polyimides.

The ternary poly(amide imide) - sulfonated PEEK - poly(ether imide) system has also been examined (two degrees of sulfonation). Sulfonated PEEK was found to act as a compatibilizing agent for the two polyimides.

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INTRODUCTION

1.1 Polymer Miscibility

The development of miscible polymer blends began with the use of butadiene/acrylonitrile rubber as a permanent plasticizer for poly(vinyl chloride), and has advanced rapidly, especially since the commercial introduction of NORYL in 1968 by General Electric. Miscible polymer blends are those mixtures of two or more chemically different polymers with a behavior (on a macroscopic level) similar to that of a single phase system. For example, a miscible blend of two polymers will exhibit a single glass transition temperature (T_g), which is usually intermediate to the T_gs of the pure components.

The phase behavior of a polymer blend depends on several factors: blend temperature and pressure, the molecular weights of each polymer, and most importantly, the chemical structures of the polymers. What may appear to be only minor differences in structure may, in fact, govern the miscibility of a blend. An example of this an effect is seen in blends of poly(methyl methacrylate) (PMMA) and poly(vinyl chloride) (PVC). For isotactic (i-) PMMA, the blends exhibit two T_gs over the entire composition range. However, syndio- tactic (s-) PMMA and PVC are miscible for blends up to the composition corresponding to a 1:1 repeat

unit ratio, with higher s-PMMA compositions exhibiting two T_gs: one corresponding to the 1:1 s-PMMA - PVC value and the other being that of pure s-PMMA (1). As the break was found to occur at such a specific composition, the authors suggested the presence of a specific interchain interaction, which cannot exist with i-PMMA. Another example of the importance of specific chemical structure was found in blends of poly-sulfones with styrene/acrylonitrile (SAN) copolymers (2). Whereas, poly(oxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy-1,4-phenyleneisopropyl-idine-1,4-phenylene) was immiscible with the SAN polymers of any composition, a slightly different poly- sulfone, poly(oxy(2,5-dimethyl-1,4-phenylene)sulfonyl(2,5-dimethyl-phenylene)oxy-1,4-phenyleneiso-propylidine-1,4-phenylene), exhibited miscibility with SAN polymers with 13-18% acrylonitrile content. Minor differences in chemical structure such as these may affect phase behavior by changing the polymer density, polarity, or solubility, by hindering or enabling rotation around certain bonds, or by shielding or exposing functional groups involved in specific intermolecular interactions.

Such intermolecular interactions are known to be thermodynamically important in polymer-polymer miscibility. In order for two polymers to be miscible, two thermodynamic criteria must be satisfied. First, the change in the free energy upon mixing (ΔG_M) must be negative,

$$\Delta G_M = \Delta H_M - T\Delta S_M < 0 \qquad (1)$$

and the second partial derivative of ΔG_M with respect to composition must be positive

$$(\delta^2 \Delta G_M / \delta \phi_i^2) > 0 \qquad (2)$$

where ϕ_i is the volume fraction of component i. Since the entropy of mixing is inversely dependent on the degrees of polymerization of the polymers, this term can be considered to be zero for high polymers. Thus, the condition that ΔG_M be negative can be approximated as

$$\Delta H_M < 0. \qquad (3)$$

The enthalpy of mixing is practically independent of degree of polymerization, but is a strong function of the contact energy of the components, i.e., energetically favorable interactions between the individual polymer molecules. Many different theories governing polymer phase behavior exist; several review articles discuss the thermodynamics of miscibility in greater detail (3-7).

Such intermolecular interactions may be of many different types. They may be classified as random dipole-induced dipole, dipole-induced dipole, dipole-dipole, ion-dipole, hydrogen bonding, acid-base or charge transfer (8). In some blends, the type of interaction and structural components involved are obvious, while in other cases, the exact nature of interactions cannot be discerned. As Olabisi, et al (8) report

> [one] must be cautioned here that the resolution of molecular interactions into the types mentioned...is to aid in the discussion of probable reasons for miscibility. With polymers, as opposed to low molecular weight compounds, the classification of an interaction can be a severe problem due partly to the extra difficulty in obtaining optimum spectroscopic results. In addition, most interactions are not quite clear-cut; there is a gray area of intermediate cases, particularly when aromatic groups or conjugated double bonds are involved.

Despite a limited understanding of polymer blend thermodynamics, polymers of nearly every type have been blended with other polymers and studied. Olabisi, et al (8) gave a (then) comprehensive survey of all miscible polymer systems. In the ten years since, new blends of existing polymers have been found, as well as blends of recently developed polymers, such as the various polyimides, poly(aryl ether sulfone)s and poly(aryl ether ketone)s.

1.2 Blends of Polyimides

Polyimides were first synthesized in 1908 by Bogert and Renshaw (9), even before the concept of "macromolecule" was commonly accepted, yet were not widely studied until the mid-1950's. These highly aromatic materials were quickly found to have excellent thermal stability, but their insolubility and infusability limited use for many years. More recently, new polyimides have been developed with flexible linkages in the main chain to promote solubility and processability, as well as to tailor specific properties such as glass transition temperature and degree (or the absence) of crystallinity. As improved processability, modification of the glass transition and changes in morphology are also achieved by physical blending, there has been wide investigation of both miscible and immiscible blends of polyimides.

Several researchers have blended polyimides with different thermoset prepolymers with varied results. Although most of this work

has been reported only in patents, some detailed studies have been published. The polyamic acid for of 4,4'-methylenedianiline and pyromellitic dianhydride was reported to be immiscible with an epoxy resin, but was found to be miscible with a phenol-formaldehyde resole prepolymer. No evidence of phase separation upon curing was found; the possibility of chemical interreaction during curing was not examined (10). Blends of a poly(ester imide) (condensation product of 1,1'-(methylenedi-1,4-phenylene)trimellitimide and ethylene glycol) and phenol-formaldehyde resins (both novolac and resole) have also been investigated. Both blends were found to be miscible in all proportions, exhibiting single, compositionally-dependent T_gs; in addition, the novolac-polyimide blends exhibited a melting point depression. Evidence of crosslinking was found for both types of blends under certain thermal conditions (11).

A poly(amide imide) synthesized from a rosin-maleic anhydride adduct has been blended with three different thermosetting resins. When blended with novolac, a window of miscibility exists for compositions in the range of 40-60% polyimide; crosslinking was found to occur above 200° C (12). In blends of this poly(amide imide) and shellac, the blends are miscible only for a 40% shellac composition, and crosslinking was again found to occur above 200° C (13). When blended with resole, only those blend compositions near 60% polyimide are miscible, and crosslinking was found to occur above 150° C (14).

Blends of poly((2,2'-bis(3,4-dicarboxyphenoxy)phenylpropane)-2-phenylene bisimide) (General Electric Co.: ULTEM 1000) and a tetraglycidyl 4,4'-diaminodiphenyl methane - diaminodiphenyl sulfone resin were reported as producing clear, homogeneous solutions in methylene chloride, but existed in separate phases after curing. The system did show improved toughness with inclusion of the poly(ether imide) (15).

Polyimides have also been blended with a number of different thermoplastic materials. A recent paper reviewed patented blend compositions of polyimides with various fluoropolymers and with many engineering and high-performance materials, such as polycarbonates, polyesters, polyamides, poly(phenylene sulfide), polybenzimidazoles, poly(aryl ether sulfone)s and liquid crystalline polymers (16). The greatest number of patents were for compositions including various poly(aryl ether ketone)s (17-34). While property claims made in the patents for these blends included improvements in mechanical properties, processability, moldability, solvent resistance, fire retardancy and abrasion resistance, only four patents explicitly stated that the blend in question is miscible or (thermodynamically) compatible (34-37).

Several researchers have examined binary blends of different polyimides. Blends of the condensation product of 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BPTA) and 4,4'-oxydianiline (ODA) and the polyimide formed from 4,4'-oxydiphthalic dianhydride (ODPA) and the same diamine were studied, with the former termed as

having "significant solubility" in the latter. Elaboration on this point, as well as experimental details, was limited (38).

Blends of two similar poly(amic acids), namely, those prepared from BPTA and either ODA or 4,4'-methylenedianiline, were studied by ultrasonic and viscometric methods (39). The results indicated that "there are two continuous regions [across the composition range] of inhomogeneity or phase separation in the blends," and that the polymers

> have limited compatibility with each other in spite of similarity in chemical structure. The fact that films of the blends are transparent at all compositions indicate that the refractive indices of both the polymers are of the same order.

The possibility of chain interreaction was not discussed. A study involving five different poly(amic acid)s reported similar findings (40). Poly(pyromellitimide)s prepared from ODA, p-phenylenediamine, and 2,2-bis(4-aminophenyl)hexafluoropropane as well as the polymer prepared from ODPA and ODA and the polymer prepared from 2,2-bis(3',4'-dicarboxyphenyl)hexafluoropropane dianhydride and ODA were used. Although the various ternary blends (two poly(amic acid)s and a solvent, N-methylpyrrolidone) "exhibited complete miscibility...as evidenced by clear mixtures," optical microscopy of the cast samples "revealed gross phase separation on a scale of several hundred microns." The samples remained phase separated after imidization. The authors suggested the possible occurence of an equilibrium, random interreaction of the two homopolymers in solution over time; this was supported by differential

mechanical thermal analysis of a series of films fully imidized after different mixing times in the ternary solution.

A recent study showed that blends of a poly(ether imide) (General Electric Co.: ULTEM 1000) and poly(oxyethyleneoxycarbonyl-2,6-naphthalenecarbonyl) (PEN) prepared in the melt state were miscible at all compositions (41). A single T_g, approximately equal to that predicted by the Fox equation (42), was reported for each composition. Mechanical properties of the blends were generally intermediate to those of the pure components; a notable exception was mold shrinkage, which was reported as having a minimum at an intermediate composition. (The mold shrinkage (percent) at the 75% PEN - 25% poly(ether imide) composition was ten percent lower than that for pure PEN, and 35 percent lower than that of the pure polyimide.)

A family of polyimide blends has recently been studied by Karasz, MacKnight and coworkers; four different polyimides, poly(ether imide) (General Electric: ULTEM 1000), the condensation product of BPTA and 5(6)-amino-1-(4'-aminophenyl)-1,3,3-trimethylindane (Ciba-Geigy: XU 218), the polyimide product of PBTA and a 4/1 molar mixture of 2,4-toluene diisocyanate and 4,4'-diphenylmethane diisocyanate (Dow Chemical: PI 2080), and the condensation product of BPTA and 3,3'-diaminobenzophenone (LaRC TPI), were all found to be miscible under certain conditions, with a polybenzimidazole (poly-2,2'(m-phenylene)-5,5'-bibenzimidazole, Hoechst Celanese: PBI) (43-45). The PBI-ULTEM

blends were reported to be miscible in all proportions (single T_g) from a first differential scanning calorimetry (DSC) heating, with values for the blend T_gs being several degrees higher than compositionally weighted values. However, two T_gs, approximately equal to those of the pure components, were observed for some compositions during the second heating scan. This phase separation was verified by optical microscopy. That a major portion of the thermodynamic phase boundary lies below the blend T_gs was suggested, with phase separation occurring only with the achievement of chain mobility at the glass transition. Improved resistance to methylene chloride and chloroform was found for these blends over the pure poly(ether imide) (43).

Blends of PBI and the XU 218 polyimide were also found to be miscible over the entire composition range, with T_gs close to the compositionally weighted averages. Values for T_g from DSC and dynamic mechanical analysis (DMA) were in close agreement. Values for T_gs increased under certain annealing conditions and were ascribed to thermally induced crosslinking. However, after annealing at 450° C, two separate T_gs were observed, indicating phase separation. DMA results confirmed the DSC data for both the crosslinking and the phase separation (43).

Due to the thermally induced changes in PI 2080 (increase in T_g from 315 to almost 400° C with annealing; crosslinking), study of the blends with PBI depended strongly on the thermal histories of the

samples (44). Despite this difficulty, single compositionally dependent T_gs were observed for all blend compositions by both DSC and DMA.

The blends of PBI - LaRC TPI were prepared using both the poly(amic acid) and 95% imidized materials, as the fully imidized polymer is insoluble. In both cases, the samples were imidized after blending according to a generally used procedure. Although LaRC TPI is known to thermally crosslink above 300° C, suggesting a kinetic dependence in the numerical values, single, compositionally dependent T_gs were observed by DSC and/or DMA for all blend compositions studied (45).

Further study of this family of blends by Fourier-transform infrared spectroscopy (FTIR) gave insight into the intermolecular interactions leading to miscibility (43-46). For the 50/50 PBI-ULTEM blend, shifts to lower wavenumbers of 3 and 4 cm^{-1} were observed for the symmetric and asymmetric stretching frequencies of the imide carbonyls, respectively; no conclusive changes in the N-H stretching region (of PBI in the blends) could be observed. The spectral changes were eliminated for blends subjected to annealing conditions known to cause phase separation. In the PBI-XU 218 blend spectra, compositionally dependent changes in the position (shifts to lower wavenumbers) and shape (broadening) were observed for the two imide carbonyl stretching bands; similar shifts in the benzophenone carbonyl band were also seen. In addition, clear shifts in the PBI N-H stretching band of up to 55 cm^{-1} were observed (46). For the PBI-PI 2080 blends, shifts in the imide

carbonyl asymmetric stretching band (up to 3 cm^{-1}) and in the N-H stretching band (up to about 40 cm^{-1}) were seen. As in the ULTEM blends, gradual reversals in these shifts were observed with annealing, suggesting lower critical solution temperature type phase behavior (44). In the PBI-LaRC TPI blends, shifts in the N-H band of up to 40 cm^{-1} were found. Well-defined shifts in the carbonyl bands (either imide or benzophenone) were not observed, although the shape of the principal imide carbonyl band was found to be skewed to lower frequencies (45). These various spectral changes suggested that PBI-PI miscibility results from specific interactions involving the >NH and carbonyl groups, found only in PBI and the polyimides, respectively (46).

Later FTIR studies of these polymers and low molecular weight monofunctional probes (47) showed that PBI was able to form hydrogen bonds with carbonyl compounds, and that the strength of these bonds was greater than in many other proton-donating polymers. It was also found that the polyimides (specifically, ULTEM and XU 218) were able to participate in hydrogen bonding through their carbonyl groups as proton-accepting polymers, but that this potential was weaker than many other polymers. Thus, the authors concluded that "in PBI/PI blend systems a hydrogen-bonding interaction occurs between the polymeric components."

Miscibility in all proportions was reported for blends of a poly(ether imide) (ULTEM) with two poly(aryl ether ketone)s: poly(oxy-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4,phenylene) (PEEK) and

poly(oxy-1,4-phenylenecarbonyl-1,4-phenylene) (PEK) (48). The PEEK-poly(ether imide) (PEI) blends possessed single, sharp T_gs, determined by DSC and dynamic mechanical testing (torsional pendulum); the values obeyed the Fox predictions within experimental error (42). Since PEEK is semicrystalline, crystalline melting peaks were observed in annealed samples. Surprisingly, no melting point depression was observed, and only a 3° C range in T_m was found. The degree of crystallinity achieved a maximum for compositions between 60-70% PEEK; this phenomenon, also found in other miscible blends with one crystallizable component, was thought to result from increased mobility in the interlamellar regions due to the presence of a completely amorphous diluent. Semicrystalline blends were reported to exhibit higher T_gs than completely amorphous blends with the same global composition due to the change in the local amorphous phase composition. Thermal analysis of the PEK-PEI blends gave similar results. No comment was made for either blend system regarding the possibility of amorphous phase separation (e.g., lower critical solution temperature type behavior).

Mechanical test results for the PEEK-PEI blends indicated that values for the tensile strength, tensile modulus and notched Izod impact strength varied monotonically with composition. However, tensile impact strength achieved a maximum at 60% PEEK; this was explained as occurring at the composition with the highest degree of PEEK crystallinity. Solvent resistance was greatly improved by blending for both organic solvents and aqueous bases. Whereas PEI, like other polyimides,

exhibits tremendous weight loss when exposed to bases, 50/50 blends with PEEK exhibited no significant losses under the same conditions.

1.3 Modifications of Poly(aryl ether ketone)s

Poly(oxy-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenylene), or PEEK, is a semicrystalline thermoplastic produced from hydroquinone and 4,4'-difluorobenzophenone. With a glass transition and a melting point at around 149° and 340° C, respectively, PEEK possesses excellent thermal stability, electrical properties and chemical and flame resistance. However, there is a sharp drop in modulus and an increased tendency to creep above T_g (49); also, the polymer is soluble at ambient conditions only in strong acids and at elevated temperatures in benzophenone, 1-chloronaphthalene, diphenyl sulfone and phenol/trichlorobenzene. A recent paper reviewed the various synthetic methods to produce, physical and solution properties and morphology of PEEK (50).

Much research has been done on the modification of PEEK. Methods for modification include physical blending, synthesis with specialty monomers or comonomers, crosslinking or post-polymerization chemical reaction.

In addition to the blends with various polyimides previously mentioned (17-34,48), patents report that PEEK has been blended with polysulfones, including poly(oxy-1,4-phenylenesulfonyl-1,4-phenylene),

poly(oxy-4,4'-biphenyleneoxy-1,4-phenylenesulfonyl-1,4-phenylene) and poly(oxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy-1,4-phenyleneisopropylidine-1,4-phenylene), polyesters, including thermotropic liquid crystalline materials, poly(phenylene oxides), including ternary blends with a poly(phenylene oxide)-polystyrene (NORYL) resin, poly(phenylene sulfide), several fluoropolymers and thermosetting materials.

Two recent studies have examined the miscibility of different poly(aryl ether ketone)s (PAEKs). In the first, a series of ten polymers with varying ketone-ether linkage ratios or isomeric forms were examined for amorphous miscibility and crystallization behavior (51). The PAEKs were reported as being miscible with others in the series within a limited range of ketone content; for example, PEEK was reported to be miscible with PEEEK, PEK, PEEKK and $P(E)_{0.43}(K)_{0.57}$ (random copolymer), but not with poly(phenylene ether) or PEKK. Crystalline behavior was also studied, with many samples reported as being isomorphic. The authors reported that

> the blends were either miscible and isomorphic or immiscible and not isomorphic. In no case was a blend found to be miscible and not isomorphic or vice versa. That immiscible blends would give rise to two melting points seems to be explained on the basis of segregated phases lacking the capability to diffuse together in order to cocrystallize....A likely explanation stems from the fact that the unit cells are so nearly identical; i.e., the [phenylene ether] and [phenylene ketone] units are so interchangeable in the crystalline lattice that if a blend is miscible in the melt so that the two types of chains can be in close proximity during crystallization it will be isomorphic.

Even though a disclaimer that "[m]ixtures of PAEKs with T_g differences of less than 10^0 C are virtually impossible to distinguish between

single phase or two-phase behavior based on T_g values" was made, several blends with such a difference in pure component T_gs were stated to be miscible. Similarly, the authors concluded that "[i]somorphism was indicated when a single melting point was detected on samples which had been cooled from the melt at 10-20° C/min". However, several of the pairs termed isomorphic had differences in pure component T_ms of less than 10° C, and one pair had a T_m difference of two degrees. No discussion was made regarding the role of kinetic effects caused by thermal history on crystallization. (The dependence of PEEK crystallization has been studied and shown to be very complex (52).)

Later work on the PEEK-PEK blend found that cocrystallization occurred only when the blends were quenched rapidly from the melt; samples which were isothermally crystallized, annealed at high temperature, cooled slowly from the melt or precipitated from solution all showed separate crystalline phases (53). The existence of amorphous miscibility based on DSC analysis alone was considered unjustified, but could be inferred by the possible occurrence of cocrystallization under certain conditions. Miscibility was seen as supported by the influence of PEK crystallites on PEEK crystallization in the blend and a slight melting point depression for PEK crystals.

Another poly(aryl ether ketone) studied in blends was poly[(3-oxo-1(3H)-isobenzofuranylidene)-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenyleneoxy-1,4-phenylene], or phenolphthalein poly(ether ether

ketone). It has been found to be miscible in all proportions with poly(hydroxy ether of bisphenol A) (phenoxy) and with polysulfone resin (54).

Modification of the properties of PEEK has also been achieved by using specialty monomers or comonomers. Poly(oxy-1,4(2-cyano)-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenylene) was prepared from 2,6-dichlorobenzonitrile; it was reported to have comparable mechanical properties, but improved solubility over PEEK (55). A series of twenty-one different PAEKs were prepared from silylated bisphenols and fluoroketones (56); values for T_gs ranged from 121° to 210° C; five of the PAEKs were reported as semicrystalline, with T_ms ranging from 223° to 306° C.

Marvel and coworkers prepared PAEKs from diphenyl ether, isophthaloyl dichloride and four isomeric biphenylene dicarboxylic dichlorides, with the isophthaloyl/biphenylene monomer ratio ranging from 19 to 99 (57). Inclusion of the biphenylene units allowed for the polymers to be thermally crosslinked when cured at 300-350° C, without the formation of volatile byproducts. A later patent covered the incorporation into PAEKs of monomers with pendant biphenylene units for crosslinking in the same manner (58).

Aromatic amine-terminated bisphenol A PAEK oligomers were found to crosslink when processed above 220° C (59). Crosslinking occurred by

reaction of the amine groups with ketone linkages to form imines. Increases in T_g after curing of 20-50° C were reported, depending on the original oligomer molecular weight.

Crosslinking has also been achieved without the inclusion of comonomers or terminal moities during polymer synthesis. For example, electron beam irradiation was found to induce crosslinking in PEEK (60). A slight increase both T_g and the shear modulus above T_g, and a decrease in T_m were reported, as well as some chain scission. Two additional methods of post-polymerization crosslinking of PEEK by reaction with crosslinking agents have been reported. Elemental sulfur (up to two percent) was used to crosslink PEEK; an increase in T_g of about 20° C, a 50% increase in modulus at 200° C and some chain scission were observed (61). PEEK crosslinked by imine formation (by the reaction of 1,4-phenylenediamine with polymer ketone linkages) was reported as having an increased T_g, dynamic storage modulus and thermal stability (62).

Four types of post-polymerization modification of PAEKs have been reported. In the first, PAEKs containing six-membered heterocycles, tricyclic-fused rings in the polymer backbone (e.g., dibenzo-p-dioxin, pheoxanthin, and thianthrene) were converted to polyamides using sodium azide (Schmidt reaction); the polyamides were found to have greatly improved solubility over the PAEKs (63).

A second modification method examined was surface fluorination (64). This was achieved by exposure of a PEEK film to an atmosphere of fluorine (5%) - nitrogen (95%). The surface tension of the film was found to increase from an original value of 30 mN/m to >54 mN/m upon treatment. No details were presented regarding chemical changes in the material.

A third post-polymerization modification of PAEKs was sulfonation. Several patents for sulfonated PAEK membranes have been granted (65-69). Sulfonated PEEKs, both in the polysulfonic acid and neutralized salt forms have been studied by Karasz, MacKnight and coworkers (70-73). They found that sulfonation in sulfuric acid placed, at most, one sulfonate group per repeat unit, that sulfonation did not occur on the phenylene rings adjacent to the carbonyl group but only on the oxy-1,4-phenyleneoxy ring, and that in sulfuric acid, sulfonation is essentially free of degradation and crosslinking reactions, provided that the acid concentration is below 100%. They also reported that the degree of crystallinity of PEEK, as determined by x-ray diffraction, was greatly decreased by sulfonation: sulfonated PEEK samples were completely amorphous, except at very low sulfonation levels.

For the free acid polymer, T_g increased monotonically with the degree of sulfonation. The neutralized salts (sodium and zinc) possessed even higher T_gs than the free acid polymer with the same sulfonation level. The thermal stability of the sulfonic acid polymer,

as characterized by thermogravimetric analysis, was significantly less than for the original PEEK; stabilities of the neutralized polymers were intermediate to the free acid and unmodified polymers. Evidence was shown that some crosslinking occurred by sulfone formation if 100% sulfuric acid was used (70).

The fourth type of post-polymerization modification was sulfonation with subsequent conversion to sulfonamides. Chlorosulfonation of several PAEKs has been carried out using either chlorosulfonic acid or sulfur trioxide/triethyl phosphate/thionyl chloride; a series of different sulfonamides was then prepared using different secondary amines (74-76). Sizeable increases in the T_gs were observed with sulfamidation, with the increases being approximately proportional to the degree of substitution, and depending strongly on the amines used. Decreases in thermal stability and in molecular weight (as determined by solution viscosity) were also found.

1.4 Overview of Dissertation

The scope of this work has been to identify and examine blends of polyimides with PEEK and chemical derivatives of PEEK. Chapter 2 presents a discussion of the three original polymers used in this study: a poly(amide imide) (PAI), a poly(ether imide) (PEI) and a poly(aryl ether ketone) (PEEK). The experimental procedures used to synthesize sulfonated, sulfamidated, nitrated and aminated PEEKs will be detailed,

as well as the preparation of the various blends examined. The methods used for characterization of these polymers and blends will be discussed.

Chapter 3 presents the analysis of the four chemically modified PEEKs; particular attention will be given to the characterization of the two polymers first prepared during this study: nitrated and aminated PEEK. Thermal and spectroscopic studies of the blends will be presented. The binary blends of PEEK-PAI and PEI-PAI have been found to be immiscible; the binary blends of sulfonated PEEK (SPEEK)-PEI, SPEEK-PAI and sulfamidated PEEK-PAI have been found to be miscible in all proportions. Nitrated PEEK-PAI blends have been found to exhibit partial miscibility. Ternary blends of SPEEK-PEI-PAI have also been studied.

Chapter 4 summarizes the results of this study and suggests future research projects based on this work.

CHAPTER 2

EXPERIMENTAL

2.1 Materials

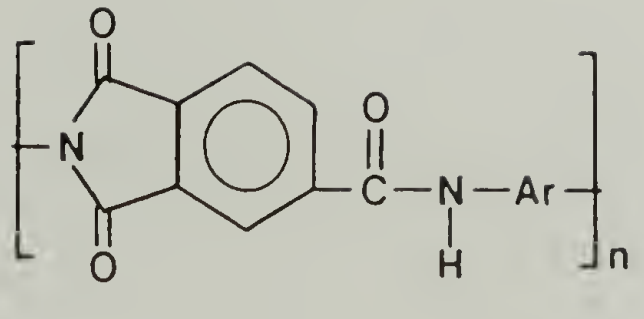
2.1.1 Polyimides

Poly(amide imide) (PAI), the condensation product of trimellitic anhydride and a 7:3 molar mixture of 4,4'-oxydianiline and m-phenylene diamine, was supplied in powder form by Amoco Chemicals Co. The polymer, commercially available as TORLON 4000T, was dried and cured at 150^0 C under vacuum for 24 hours prior to use, as recommended by the manufacturer. The chemical structure of PAI is shown in Figure 2.1.

Poly(2,2'-bis(3,4-dicarboxyphenoxy)phenylpropane)-2-phenylene bisimide) (ULTEM 1000, PEI) was supplied by General Electric Co., Pittsfield, Massachusetts, in the form of pellets. The resin is commercially available as ULTEM 1000. The chemical structure of PEI is shown in Figure 2.2.

2.1.2 Poly(ether ether ketone)

Poly(ether ether ketone) (PEEK) powder, commercially available as VICTREX PEEK 38P, was supplied by ICI, Wilton, England. The



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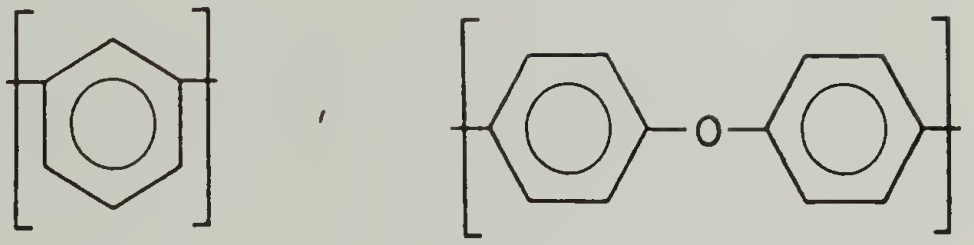

Figure 2.1. Chemical structure of poly(amide imide) (PAI).

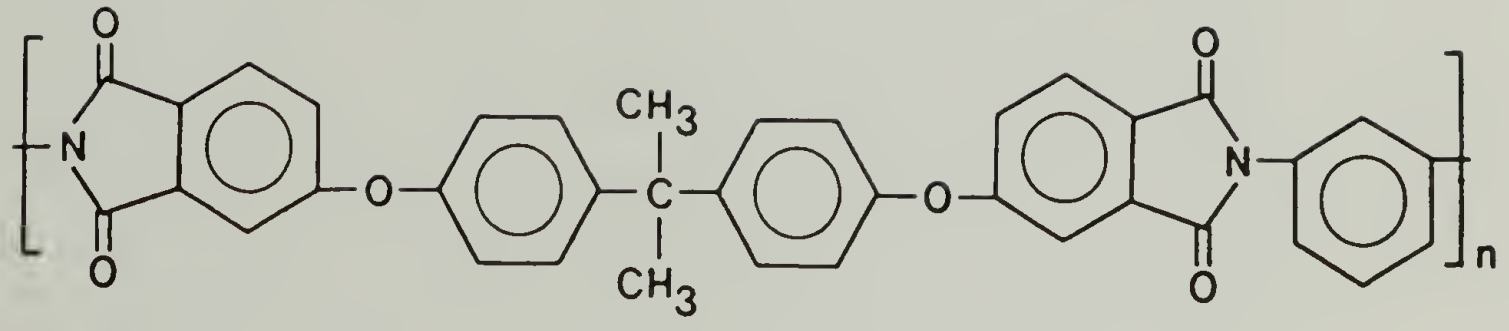

Figure 2.2. Chemical structure of poly(ether imide) (PEI).

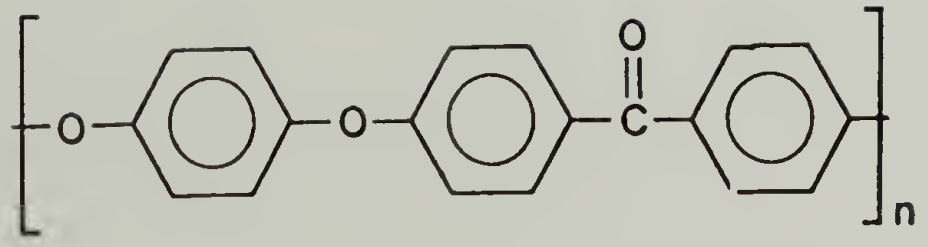

Figure 2.3. Chemical structure of poly(ether ether ketone) (PEEK).

manufacturer reported the $\bar{M}_n$ and $\bar{M}_w$ as 14,100 and 38,600, repectively. The chemical structure of PEEK is shown in Figure 2.3.

2.1.3 Reagents and Solvents

Sulfonations of PEEK were carried out using as-received sulfuric acid (assay 95.0%, Fisher Scientific). For preparation of sulfamidated PEEK, chlorosulfonic acid (assay 99.9%, EM Sciences) and piperidine (99%, Aldrich) were used as received. Nitration utilized as-received nitric acid (assay 69.0-71.0%, Fisher Scientific).

Reagents used for the reduction of nitrated PEEK were stannous chloride (98%, Fisher), hydrochloric acid (A.C.S. reagent, assay 36.5-38.0%, Fisher), sodium sulfide nonahydrate (reagent grade, Fisher), sulfur (Fisher), and glacial acetic acid (assay 99.7%, Mallinckrodt); all were used as received. Zinc dust (certified, Fisher) was purified by washing in 2% (w) hydrochloric acid, collected by filtration, washed twice more with the same acid, then four times in a large excess of water.

The principal solvents used in blend preparation were methanesulfonic acid (MSA) (99%, Aldrich) and dimethyl acetamide (DMAc) (certified, Fisher); both were used as received. All additional solvents used for determination of the solubility of nitrated and aminated PEEKs were reagent grade or better, and were used as received.

The water used for all precipitations, washings and for solubility determinations was twice distilled.

2.1.4 Chemical Derivatives of PEEK

2.1.4.1 Sulfonated PEEK

Procedures used for the controlled sulfonation of PEEK were based on those developed in previous studies (70-73). Polymers of three levels of sulfonation were prepared. For the first, PEEK powder was dissolved in sulfuric acid (conc. = 20.0 mg/ml) and stirred at room (25 ± 3^{0} C) temperature for 35 hours. The resulting sulfonated polymer was precipitated by dropwise addition of one part solution to four parts water, with the mixture chilled during the precipitation process. The polymer was collected by filtration and washed thrice thoroughly with water to completely remove any remaining acid. For the second sulfonation, PEEK powder was dissolved in sulfuric acid at the same concentration and stirred at room temperature for 36 hours; the third sulfonated polymer was prepared by dissolution in sulfuric acid at the same concentration and stirred at 35^{0} C for 200 hours. These polymers were precipitated, filtered and washed in the same fashion. The sulfonated PEEKs (SPEEKs) were dried under vacuum at 100^{0} C for 24 hours; rigorous drying was necessary due to the hygroscopic nature of SPEEK. The polymers were stored in a vacuum desiccator over calcium sulfate until used.

2.1.4.2 Sulfamidated PEEK

The procedure used to prepare the chlorosulfonated and sulfamidated PEEK (SAPEEK) was based on those developed by Marvel and coworkers (74-76). PEEK powder was dissolved in chlorosulfonic acid (conc. = 100.0 mg/ml) and stirred at room temperature for 48 hours. The chlorosulfonated polymer was precipitated by dropwise addition of one part solution to twenty parts chilled water; it was collected by filtration, washed with water to remove residual acid, shredded in a blender and washed an additional three times with water. The chlorosulfonated PEEK was dried at 100° C under vacuum before further reaction.

To prepare the sulfonamide, 1.800 g of the chlorosulfonated polymer was slurried in 50.0 ml of 1,2-dichloroethane at room temperature; 10.00 ml of piperidine were added, and the mixture stirred for five hours. To recover the polymer, the emulsionlike solution was poured into a large excess of methanol. The polymer was collected by filtration, washed thrice with methanol, shredded, washed twice more with methanol, dried at 80° C under vacuum for fifteen hours and stored in a vacuum desiccator over calcium sulfate until used.

2.1.4.3 Nitrated PEEK

Polymers with five different degree of nitration were prepared; the degree of nitration of the polymer was controlled by varying the

quantity of nitric acid introduced. Samples of PEEK powder were dissolved in methanesulfonic acid (MSA) (conc. = 50.0 mg/ml), and stirred at room temperature until completely dissolved (approximately 24 hours); the solutions were deep red and transparent. Separately, a certain volume of nitric acid and an equal volume of MSA were mixed and allowed to equilibrate for fifteen minutes. Ratios of the volume (in milliliters) of nitric acid to amount (in grams) of PEEK were (1) 0.10, (2) 0.20, (3) 0.25, (4) 0.50 and (5) 0.75. The acid mixtures were added dropwise to the respective polymer solutions, with continued stirring to ensure homogeneity. Upon addition of the nitric acid, the colors of the solutions gradually changed from red to brown. Precipitation was observed for sample (4) and (5) (highest nitric acid/PEEK ratios). In sample (4), a small amount of yellow precipitate evolved over time, and the solution became cloudy; for sample (5), a larger amount of yellow precipitate appeared within five minutes of the addition of the nitric acid, and the entire solution became opaque. No precipitation was observed in the other three polymer solutions (lowest nitric acid/PEEK ratios). Stirring was continued for thirty minutes after the addition of the nitric acid.

Complete precipitation of each polymer from solution was achieved by dropwise addition of the solution to water (volume ratio of water to acid: > 5:1), with the mixtures being chilled during precipitation. The polymer was collected by filtration, washed with a 50:50 (v/v) mixture of water and methanol to remove any acid, shredded in a blender as

needed, and washed three additional times with the same aqueous mixture. The nitrated poly(ether ether ketone)s (NPEEKs) were dried under vacuum at 100° C for 24 hours, then stored in a vacuum desiccator over calcium sulfate until used.

2.1.4.4 Aminated PEEK

Methods used for reducing aromatic nitro compounds to amines are limited by the presence of other functional groups and by the nature of the reaction (homogeneous or heterogeneous). Three different methods of reduction of NPEEK were studied: $SnCl_2/HCl$, Na_2S_x (Zinin reaction) and Zn/Ch_3CO_2H.

Stannous chloride - hydrochloric acid has been used in the reduction of nitrobenzaldehyde to the corresponding amine without affecting the aldehyde group (77). Stannous chloride dihydrate (3.44 g) was dissolved in hydrochloric acid (12.5 ml); 1.00 g of NPEEK (degree of nitration = 0.82 nitro groups per polymer repeat unit) was added and vigorously stirred for several hours. The slurry was then heated to 50-55° C for 24 hours. Upon removal from the heat, the polymer was precipitated into a large excess of water, filtered, washed with water repeatedly to remove any residual reagents, and dried for 24 hours at 100° C under vacuum. The polymer was then stored in a vacuum desiccator over calcium sulfate until used.

Sodium sulfide has been reported as an effective reducing agent for nitro groups in the presence of other functional groups (78); it has also been utilized in the reduction of poly(4-amino-3-nitrostyrene) to poly(3,4-diaminostyrene) (79). Sodium polysulfide was prepared by mildly heating a mixture of 1.202 g sodium sulfide nonahydrate, 0.290 g sulfur and 5.00 ml water. A 1.00 ml portion of this clear orange liquid was added to a slurry of 1.00 g NPEEK in 75.0 ml water. The mixture was vigorously stirred and refluxed under a nitrogen atmosphere for 100 hours. The slurry was filtered immediately upon removal from the heat, washed repeatedly with water to remove any residual reagents, dried for 24 hours at 100° C under vacuum and stored in a vacuum desiccator over calcium sulfate until used.

Zinc metal - acetic acid have been reported as reagents for the reduction of nitro groups in the presence of other functional groups, and also for nitro reduction in heterogeneous media (80a,b). Zinc dust (1.30 g) was purified, and was then mixed with 1.00 g NPEEK; 30.0 ml water was added to the blend to form a thick paste. Separately, 0.25 ml of acetic acid and 0.75 ml water were mixed and allowed to equilibrate. The diluted acid was added to the paste with an additional 20.0 ml of water; the mixture was gradually heated to 65° C with continuous stirring. After 24 hours, the polymer was removed from the heat and filtered immediately. The solids were placed in approximately 100 ml of water to allow the remaining zinc to settle out; the polymer was later decanted from this fluid. The recovered polymer was finely ground, and

the procedure repeated twice to remove any remaining zinc. The polymer was washed twice more with water, dried for 24 hours at 100° C under vacuum, and stored in a vacuum desiccator over calcium sulfate until used.

2.2 Blends

2.2.1 PEEK - Poly(amide imide)

Poly(ether ether ketone) is known to be readily soluble at ambient conditions and without chemical reaction in MSA. Poly(amide imide) was found to be soluble in this acid as well. The chemical composition of a PAI sample precipitated from MSA (determined by elemental analysis) showed no significant difference from the composition of a control sample of the polymer; also, the glass transition temperatures and the heat capacity changes at the glass transition (ΔC_p) were found to be the same for the original and precipitated materials. These results indicate that no chemical changes to the polymer occurred, and that MSA acts only as a solvent for PAI.

Blends of the two polymers were prepared by mixing MSA solutions (conc. = 10.0 mg/ml) of each polymer in the desired proportions. These solutions were stirred at room temperature until homogeneous. All of the blend solutions were observed to be clear and were brown in color. The polymers were coprecipitated by dropwise addition of one part

solution to four parts of a chilled, 50/50 (v/v) mixture of methanol and water. The blends were collected by filtration, washed four times with the same methanol/water mixture to remove residual acid, and dried at 100° C for 40 hours under vacuum. The blends were stored in a vacuum desiccator over calcium sulfate until analysis.

2.2.2 Poly(ether imide) - Poly(amide imide)

Both polyimides are readily soluble in dimethyl acetcamide (DMAc) at ambient conditions. Blends were prepared by mixing DMAc solutions (conc. = 10.0 mg/ml) of each polymer in the desired proportions, with these solutions being stirred until homogeneous. Films of the blends were obtained by casting the solutions into aluminum pans, and placing them in an oven at 155° C under vacuum for 36 hours to remove the solvent. The blend samples were then removed to a vacuum desiccator and stored over calcium sulfate until analyzed.

2.2.3 Sulfonated PEEK - Polyimide

2.2.3.1 Binary

The sulfonated PEEKs (all degrees of sulfonation) prepared were soluble in DMAc. Similar procedures were used for the preparation of the binary SPEEK-PEI and SPEEK-PAI blends of each degree of sulfonation. Blends were prepared by mixing DMAc solutions (conc. = 40.0 mg/ml) of

each sulfonated PEEK and the respective polyimides in the desired proportions. The solutions for the SPEEK (X_S = 0.42) blends were stirred at approximately 80° C until homogeneous; blend solutions for each of the other two SPEEK materials were stirred at room temperature until homogeneous. All of the blend solutions were observed to be clear; as is characteristic of polyimides, the solutions were amber in color.

Films of the blends were prepared by casting the solutions into aluminum pans. For the SPEEK (X_S = 0.42) blends, the solvent was removed by drying for 24 hours at 120° C under vacuum. The temperature was then gradually raised to 175° C, and the samples held at this temperature for an additional 24 hours to remove any remaining solvent. For the other SPEEK blends (X_S = 0.53 and 1.00), the procedure was nearly identical with the single difference being that the samples were dried at 100° C under vacuum for the first 24 hour period, rather than 120° C. Upon the completion of this procedure, all the blend samples were stored in vacuum desiccators over calcium sulfate until analysis. Transparent, amber films were obtained over the entire composition range for blends of all three sulfonated PEEKs with each of the polyimides.

2.2.3.2 Ternary

Ternary blends were comprised of the poly(amide imide), the poly(ether imide) and a sulfonated PEEK. Ternary blend samples were

prepared for each of the two SPEEKs (different degrees of sulfonation). The ternary blends were prepared by the same procedure as the corresponding binary SPEEK-polyimide blends of the same degree of sulfonation with the single exception that the original solutions of the polymers were of a concentration of 20.0 mg/ml, rather than 40.0 mg/ml.

2.2.4 Sulfamidated PEEK - Poly(amide imide)

Sulfamidated PEEK was found to be readily and completely soluble in DMAc. Blends of the sulfonamide with PAI were prepared by mixing DMAc solutions (conc. = 20.0 mg/ml) of the polymers in the desired proportions. The blend solutions were stirred at room temperature until homogeneous; all solutions were observed to be clear and amber in color.

Films were prepared by casting into aluminum pans. Solvent was removed by drying for 24 hours at 100° C and then an additional 24 hours at 170° C, all under vacuum. The blend samples were stored in a vacuum desiccator over calcium sulfate until analysis.

2.2.5 Nitrated PEEK - Poly(amide imide)

The nitrated PEEKs with the three highest degrees of nitration were blended with PAI for study. These three NPEEKs were readily and completely soluble in DMAc. Blends were prepared by mixing solutions (conc. = 20.0 mg/ml) of PAI and each NPEEK in the desired proportions

and stirring until homogeneous. All solutions for each NPEEK were clear and amber in color. Films were prepared in the same manner as for the sulfonated PEEK and sulfamidated PEEK blends with the exception that the temperatures used during solvent removal were 100° C (24 hours), then 130° C (24 hours). The NPEEK blends were stored in the same fashion as all the other blends.

2.3 Characterization Methods

2.3.1 Elemental Analysis

Elemental analyses of various polymers in this study were performed by the University of Massachusetts Microanalysis Laboratory according to generally used procedures (81). Carbon, hydrogen and nitrogen analyses were conducted using a Control Equipment Corp. Elemental Analyzer, utilizing a modified Pregl-Dumas (combustion) technique. Oxygen analyses were conducted using the same instrument and a modified Unterzaucher method. The analyses for sulfur were made according to the standard Association of Official Analytical Chemists (AOAC) procedure 47.040; this method involved sample decomposition in a Schoniger oxygen (closed) flask, with titration of the resulting sulfate with barium. Chlorine determination was made according to AOAC method 47.007 using a Schoniger decomposition, and subsequent coulometic titration of the chloride with silver.

2.3.2 Spectroscopy

2.3.2.1 Fourier-Transform Infrared Spectroscopy

The infrared spectra were obtained using an IBM IR/32 FTIR instrument with continuous dry nitrogen purge during scanning. The spectra were taken at room temperature in the range of 4000-400 cm^{-1} with 2 cm^{-1} resolution, and were signal averaged from at least 200 scans. All samples were prepared by casting from DMAc onto KBr pellets; the polymer solutions were heated as necessary to achieve sufficient solubility for casting.

2.3.2.2 Nuclear Magnetic Resonance

The carbon-13 nuclear magnetic resonance measurements were performed using a Varian XL-300 spectrometer with broad band proton decoupling at 60° C. The polymer solution was 2% (w/w) in DMSO-d6; the solvent carbon peak at 39.6 ppm as a reference (solvent peak position relative to tetramethylsilane).

2.3.2.3 Ultraviolet Spectroscopy

The ultraviolet spectroscopic measurements were performed at room temperature using a Beckman UV-7 Spectrophotometer in absorbance mode. Spectra of PAI, PEI and SPEEK (X_S = 0.53 and 1.00), as well as 50/50 (w)

blends of each polyimide with each SPEEK were obtained from DMAc solutions at room temperature, relative to the pure solvent background. Total polymer concentrations of all the solutions were 0.000500 mg/ml; absorbance values obtained for the blends were corrected for comparison with the pure component spectra.

Spectra were obtained in the 250-315 nm wavelength range. The range of interest was limited by the pure solvent absorbance; polymer solution concentrations were limited to those used in order to obtain the most precise spectra in this wavelength window. Above 315 nm, the difference between the polymer solutions and the pure solvent background were minimal and not reproducible.

2.3.3 Thermal Analysis

2.3.3.1 Differential Scanning Calorimetry

The glass transition temperatures (T_g) and melting behaviors of the polymers and blends were determined by differential scanning calorimetry (DSC), using a Perkin-Elmer DSC-4. Calibrations for temperature and heat flow were made prior to sample analysis using indium, tin and zinc samples. Samples (4-12 mg) were heated under nitrogen at a scanning rate of 20° C/min from 50° C to a variable upper limit, depending on the polymer(s). Upper temperature limits were 400° C for virgin PEEK and the PEEK-PAI blends, 350° C for the PEI-PAI blends, 325° C for all of

the sulfonated PEEK binary and ternary blends, 300° C for the five nitrated PEEKs, nitrated PEEK-PAI blends, sulfamidated PEEK and sulfamidated PEEK-PAI blends, and 250° C for the aminated PEEK. All samples were scanned twice to allow for the removal of residual water, with results determined from the second heating scan. Error limits for the glass transition temperatures were ±3° C.

2.3.3.2 Thermogravimetric Analysis

Thermogravimetric analyses (TGA) were carried out using a Perkin-Elmer TGS-2, with a heating rate of 20° C/min in the range of 50-850° C. Sample sizes were approximately 5-10 mg; a helium atmospshere was used for all samples.

Exploration of the mechanism of degradation of nitrated PEEK was carried out for the NPEEK sample with the highest degree of nitration. A partially degraded sample was prepared by using the TGS-2 (heating rate = 20° C/min; helium atmosphere) in the range of 50-450° C; the chemical composition of the resulting material was determined by elemental analysis.

2.3.4 Solubility

The solubilities of all five nitrated PEEKs and the aminated PEEK were determined in fourteen common solvents. Conditions for determining

solubility were at a concentration of 1% (w/v) and at room temperature. Solvents studied were (in order of increasing Hildebrand solubility parameter): toluene, chloroform, chlorobenzene, acetone, nitrobenzene, m-cresol, pyridine, dimethyl acetamide, dimethyl sulfoxide, dimethyl formamide, benzyl alcohol, formic acid, methanol and water.

2.3.5 Solution Viscosity

Solution viscosity measurements were made using Ubbelohde viscometers, and were conducted in a temperature bath at 26.00±0.25° C. For each pure solvent and polymer concentration, 4-7 measurements were made, with averaged values used in calculations. Intrinsic viscosities were calculated by taking the limit of the inherent viscosities as the polymer concentration was extrapolated to zero; four different polymer concentrations were studied: 0.150, 0.200, 0.250 and 0.300 dl/g. Viscosities were also determined in the same fashion for the as-synthesized SPEEK and for a SPEEK sample which had been annealed at 300° C for five minutes.

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Synthesis and Characterization

3.1.1 Sulfonated PEEK

The sulfonated PEEKs were recovered in the form of yellow powders, with the probable cause of the color being self-protonation of the carbonyl groups (70). The degrees of sulfonation (X_S), defined as the average number of sulfonic acid groups per polymer repeat unit (as shown in Figure 2.3), were determined from the sulfur/carbon ratio of each sample. The degree of sulfonation was 0.42 for the first synthesis (ambient temperature, 35 hours), 0.53 for the second (ambient temperature, 36 hours) and 1.00 for the third (35° C, 200 hours). The glass transition temperatures were determined to be 182° C (X_S = 0.42), 191° C (X_S = 0.53) and 205° C (X_S = 1.00); these values are in general agreement with those reported by Jin, et al (71). This increase in T_g with sulfonation, which was found to be proportional to the square root of the degree of sulfonation, can be understood as resulting from two factors: polar/ionic interactions involving the sulfonic acid groups and general hindered rotation along the chain caused by the introduction of the bulky $-SO_3H$ groups (71).

The breadth of the DSC glass transitions were also found to increase with higher levels of sulfonation. This is a result of increasing heterogeneity and intermolecular interactions in the polymers; such broadening is expected, since the sulfonation of PEEK produces a type of copolymer.

The SPEEK (X_S = 0.53) sample annealed at 300° C for five minutes showed no noticable color change from the non-annealed polymer. The annealed sample was found to also be completely soluble in DMAc at room temperature. The intrinsic viscosities of the polymers before and after annealling were found to be in good agreement: 1.65 dL/g for the original polymer and 1.64 dL/g for the annealed. This suggests the absence of degradation or crosslinking reactions under these conditions; however, such reactions may occur as a result of more severe time/temperature exposure.

The SPEEK materials were all found to be completely soluble in DMAc. The two more highly sulfonated polymers were readily soluble at room temperature, while the third polymer (X_S = 0.42) was soluble only in DMAc only upon heating.

3.1.2 Sulfamidated PEEK

The sulfamidated PEEK was recovered in the form of a white powder. The degree of sulfamidation (X_{SA}), defined as the average number of

sulfonamide groups per polymer repeat unit, was calculated from the sulfur/carbon ratio of the chlorosulfonated PEEK, and the sulfur/carbon and nitrogen/carbon ratios of the sulfamidated polymer; the arithmetic mean of the ratios (1.34, 1.28 and 1.38, respectively) gave an average degree of sulfamidation of 1.33. (Similar variation in the elemental ratios were observed for other sulfamidated poly(aryl ether ketone)s (74,76).) The sulfamidated PEEK was found to be readily and completely soluble in DMAc at ambient conditions. The glass transition temperature was determined to be 215° C. Results of thermogravimetric analysis are shown in Figure 3.1; the onset of degradation temperature (in helium) was 329° C.

The chlorosulfonation of PEEK was found to proceed at a higher rate than for the chlorosulfonation of other poly(aryl ether ketone)s, such as poly(oxy-1,4-phenylenecarbonyl-1,3-phenylenecarbonyl-1,4-phenylene) (iPEKK) and poly(oxy-1,4-phenylenecarbonyl-1,4-phenylenecarbonyl-1,4-phenylene) (tPEKK) (74,76). For example, chlorosulfonation of iPEKK at 60° C for 96 hours and a concentration of 1.2 mg polymer/ml acid yielded a polymer with a degree of substitution of 0.61, compared to a degree of substitution of 1.33 as found in this study (25° C, 48 hours, conc. = 1.0 mg PEEK/ml acid). The higher rate may result from the differences in the electronic character of the phenylene rings of the two polymers. In PEEK, the oxy-1,4-phenyleneoxy ring is more reactive toward electrophiles than the two rings adjacent to the carbonyl (e.g., as demonstrated in sulfonation in sulfuric acid (71)). This ring is likely

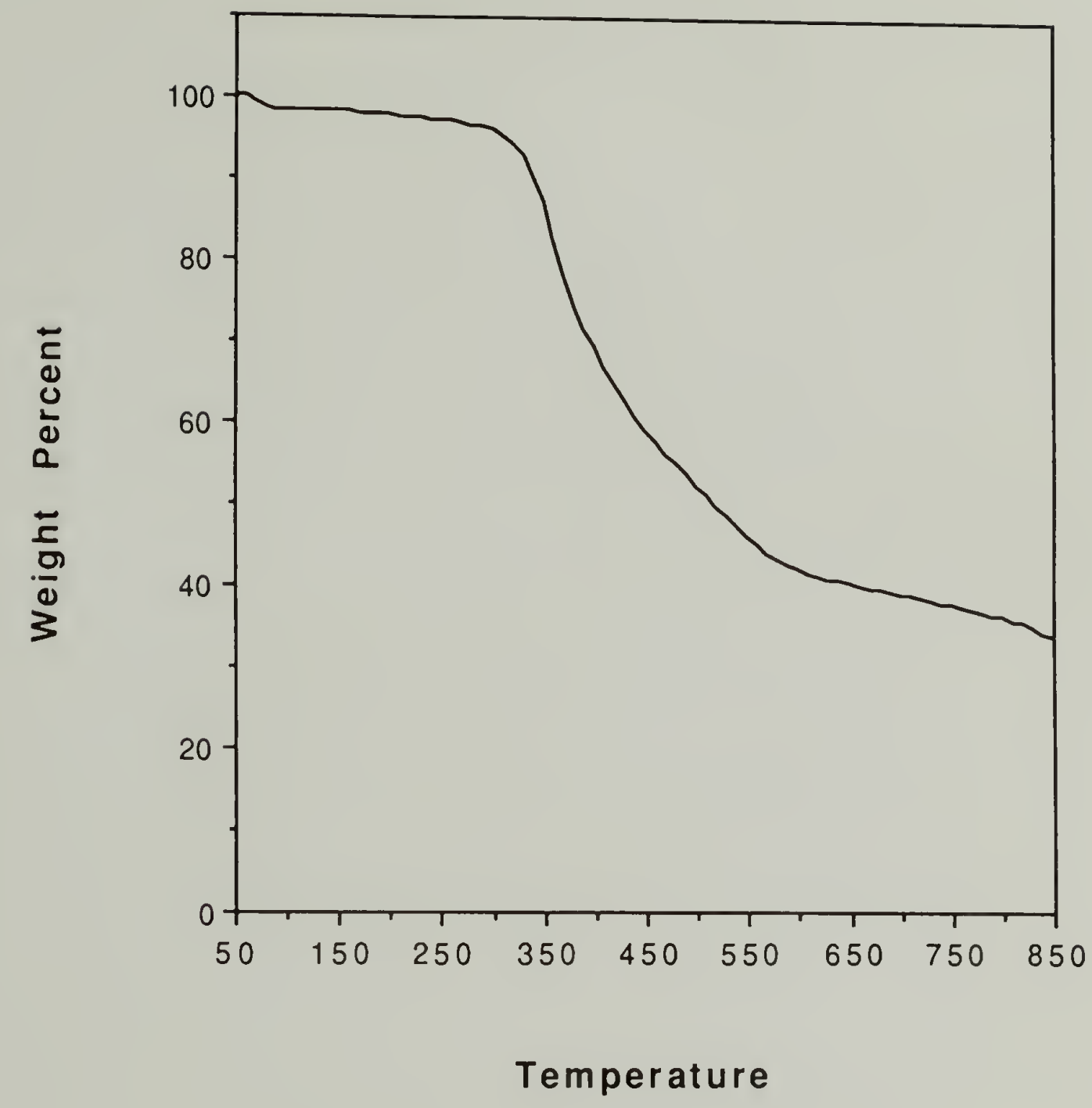

Figure 3.1. Thermogravimetric analysis of sulfamidated PEEK.

the initial site for substitution in chlorosulfonic acid, but with subsitution occurring on the other two rings as well (70).

3.1.3 Nitrated PEEK

The nitrated PEEKs were recovered as pale pink-orange powders, with the polymer color changing gradually (from pink to orange) according to the original nitric acid volume - PEEK mass ratio. The degrees of nitration (X_N), defined as the average number of nitro groups per polymer repeat unit, were calculated from the nitrogen/carbon ratios of the products; the results are shown in Table 3.1.

Table 3.1 Degree of Nitration

sample	volume, nitric acid (ml)/PEEK (g)	$\bar{X}_N$
(1)	0.10	0.42
(2)	0.20	0.82
(3)	0.25	1.15
(4)	0.50	2.15
(5)	0.75	2.79

The room temperature solubilities of the five different NPEEKs in fourteen common solvents were determined. The results are given in Table 3.2.

Table 3.2 Solubility of Nitrated PEEKs

solvent	solubility parameter	Degree of Nitration 0.42	0.82	1.15	2.15	2.79
toluene	8.9	I	I	I	I	I
chloroform	9.3	SW	PS	PS	I	I
chlorobenzene	9.5	I	I	I	I	I
acetone	9.9	I	I	I	I	I
nitrobenzene	10.0	SW	PS	S	S	S
m-cresol	10.2	SW	PS	S	PS	SW
pyridine	10.7	I	SW	S	S	S
dimethyl acetamide	10.8	SW	PS	S	S	S
dimethyl sulfoxide	12.0	I	PS	PS	S	S
dimethyl formamide	12.1	I	I	PS	S	S
benzyl alcohol	12.1	I	I	I	I	I
formic acid	12.1	I	I	I	I	I
methanol	14.5	I	I	I	I	I
water	23.4	I	I	I	I	I

I = Insoluble
SW = Swollen
PS = Partially Soluble
S = Soluble

Solvent solubility parameter in $(cal/cm^3)^{1/2}$

The parent polymer, PEEK, is only soluble at room temperature in strong acids, and soluble in non-protonating solvents (e.g., benzophenone, 1-chloronaphthalene, phenol/1,2,4-trichlorobenzene (50/50 mixture by weight), diphenyl sulfone) at high temperatures (>190° C). It is completely insoluble in the seven solvents resulting in partial or full solubility of the NPEEKs. Since the strong intercrystalline forces and the limited polarity of PEEK lead to its near-total insolubility, nitration apparently disrupts the chemical nature and the structural regularity of the polymer chains to such a degree as is necessary for greatly enhanced solubility. These changes in the chemical structure show, as expected, a clear dependence on the degree of nitration; the NPEEK with $X_N = 0.42$ carries a nitro substituent on an average of one of every seven phenylene (global) rings, while the polymer with $X_N = 2.79$ has nearly one-to-one average substitution.

Although a clear assignment of a solubility parameter value cannot be made, a range of 10.0-12.0 $(cal/cm^3)^{1/2}$ seems reasonable, with the specific value of the parameter increasing within this range with higher degrees of nitration. This compares to a theoretical amorphous value of 10.5 for PEEK, as determined using Small's method (82), and NPEEK values of approximately 10.6 ($X_N = 0.42$) and 11.0 ($X_N = 2.79$).

As with most polymers, though, a single solubility parameter does not completely define NPEEK solubility. An example is seen with the three solvents which all have solubility parameters of 12.1 (dimethyl

formamide (DMF), benzyl alcohol and formic acid); all of the NPEEKs were insoluble in the latter two solvents; the X_N = 0.42 and 0.82 polymers are insoluble, the X_N = 1.15 polymer partially soluble and the X_N = 2.15 and 2.79 polymers completely soluble in DMF. A closer examination of NPEEK solubility indicated an important trend; with the exception of nitrobenzene, for which NPEEK solubility can presumably be explained by the adage "like dissolves like", the solvents which swell or dissolve the five NPEEKs can all be classified as polar and nucleophilic. Thus, the interactions between polymer and solvent leading to swelling and dissolution observed here can be explained as electronic interactions between nucleophilic and electrophilic (the nitrated phenylene rings of the polymer) moities. This was confirmed by examination of the colors of the polymer solutions; the X_N = 1.15/m-cresol solution was found to be orange, the pyridine solutions were orange-red (X_N = 1.15, 2.15 and 2.79), and the DMAc (X_N = 1.15, 2.15, 2.79), DMSO and DMF (X_N = 2.15, 2.79, each) solutions were yellow, even though these solvents, in pure form, were all colorless. (The nitrobenzene solutions showed no color change with respect to the pure solvent.)

The change in the electronic nature of the polymers with increasing degree of nitration also serves to explain the precipitation observed during some of the nitration reactions. Since the dissolution of PEEK in MSA can be attributed to protonation of the polymer (confirmed by the deep red color of such solutions), the polymer acts as a nucleophile in this solution. Nitration of a phenylene ring in the polymer converts

the ring from a (potential) nucleophile to an electrophile. With increasing nitration of a given chain, the number of possible protonation sites is decreased until a certain threshold number of rings (protonation sites) are nitrated. At this point, sufficient interactions between the polymer and the solvent to keep the chain in solution no longer exist, and precipitation begins. This explains why no precipitation was observed for three of the NPEEKs syntheses (X_N = 0.42, 0.82, 1.15), and why partial (X_N = 2.15) and nearly complete (X_N = 2.79) precipitation was observed at higher levels of nitration.

The infrared spectra of four of the nitrated PEEKs are shown in Figures 3.2 to 3.5. (A strong spectrum of the least nitrated NPEEK (X_N = 0.42) could not be obtained due to that polymer's very limited solubility.) Nitration can be expected to significantly alter the absorption pattern of PEEK (83) with the rise of $-NO_2$ (asymmetric and symmetric) and C-N stretching bands, variations in the aromatic C-H out-of-plane bending patterns (due to new aromatic substitution) and splitting of the ketone and ether bands. Several of these changes were clearly observed and definitely assigned; other smaller changes were also observed, but definite assignments could not be made due to overlapping of vibrational modes.

The first clear difference observed when comparing spectra of the substituted and unsubstituted polymers was the emergence of peaks at 1535 and 1349 cm^{-1} for the nitrated polymers; these absorptions were

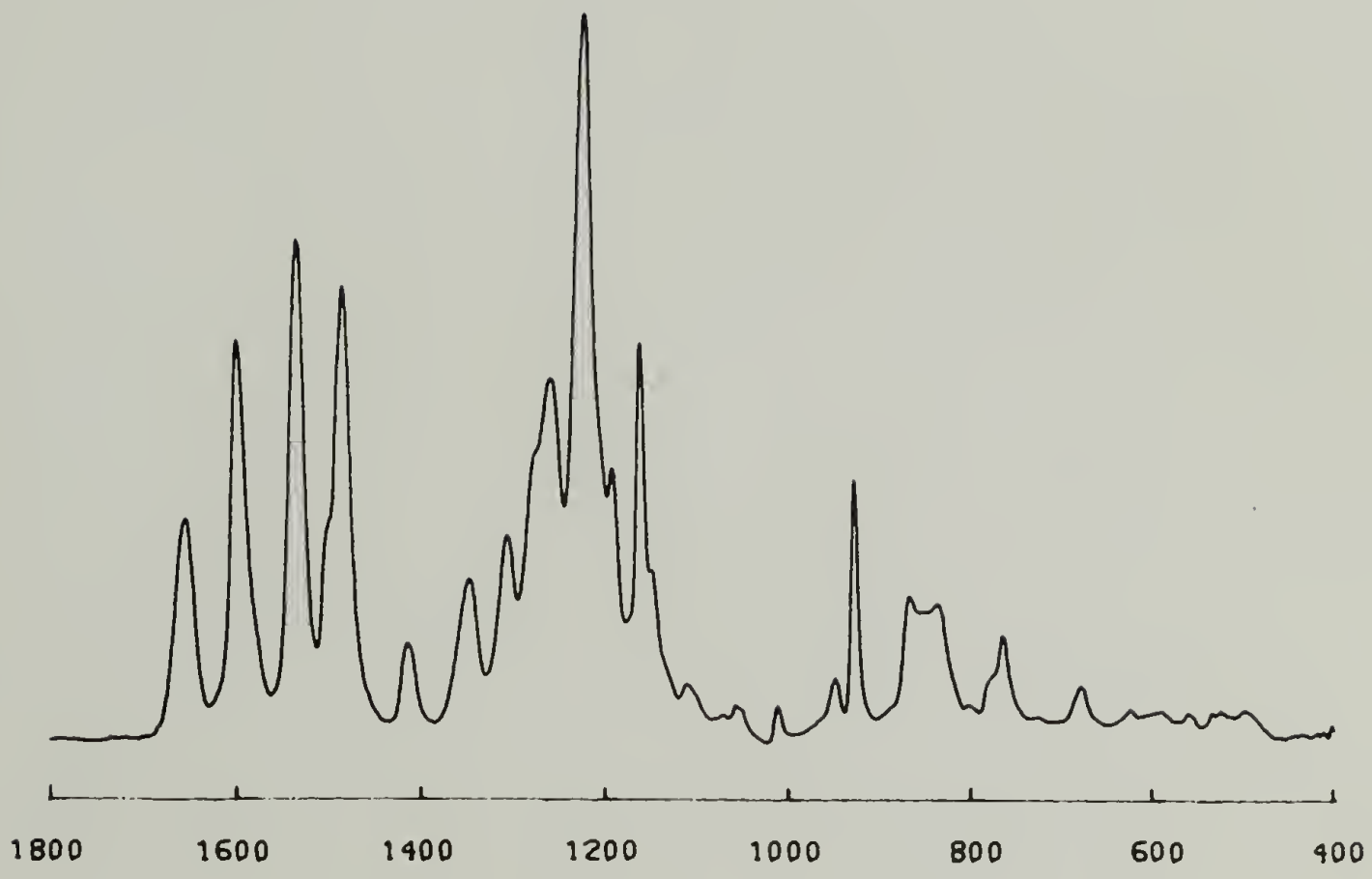

Figure 3.2. Fourier-transform infrared spectrum of nitrated PEEK (degree of nitration = 0.82).

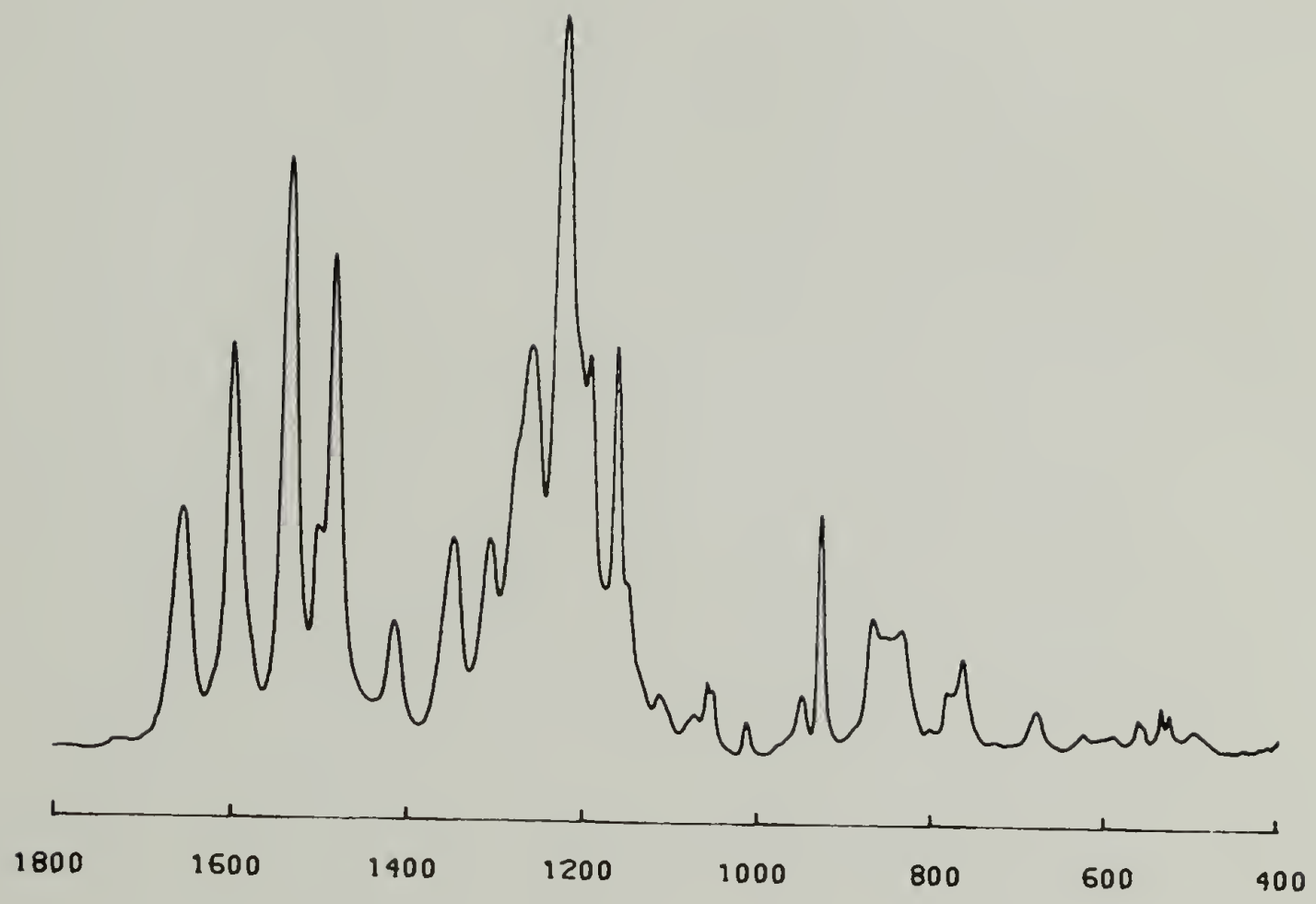

Figure 3.3. Fourier-transform infrared spectrum of nitrated PEEK (degree of nitration = 1.15).

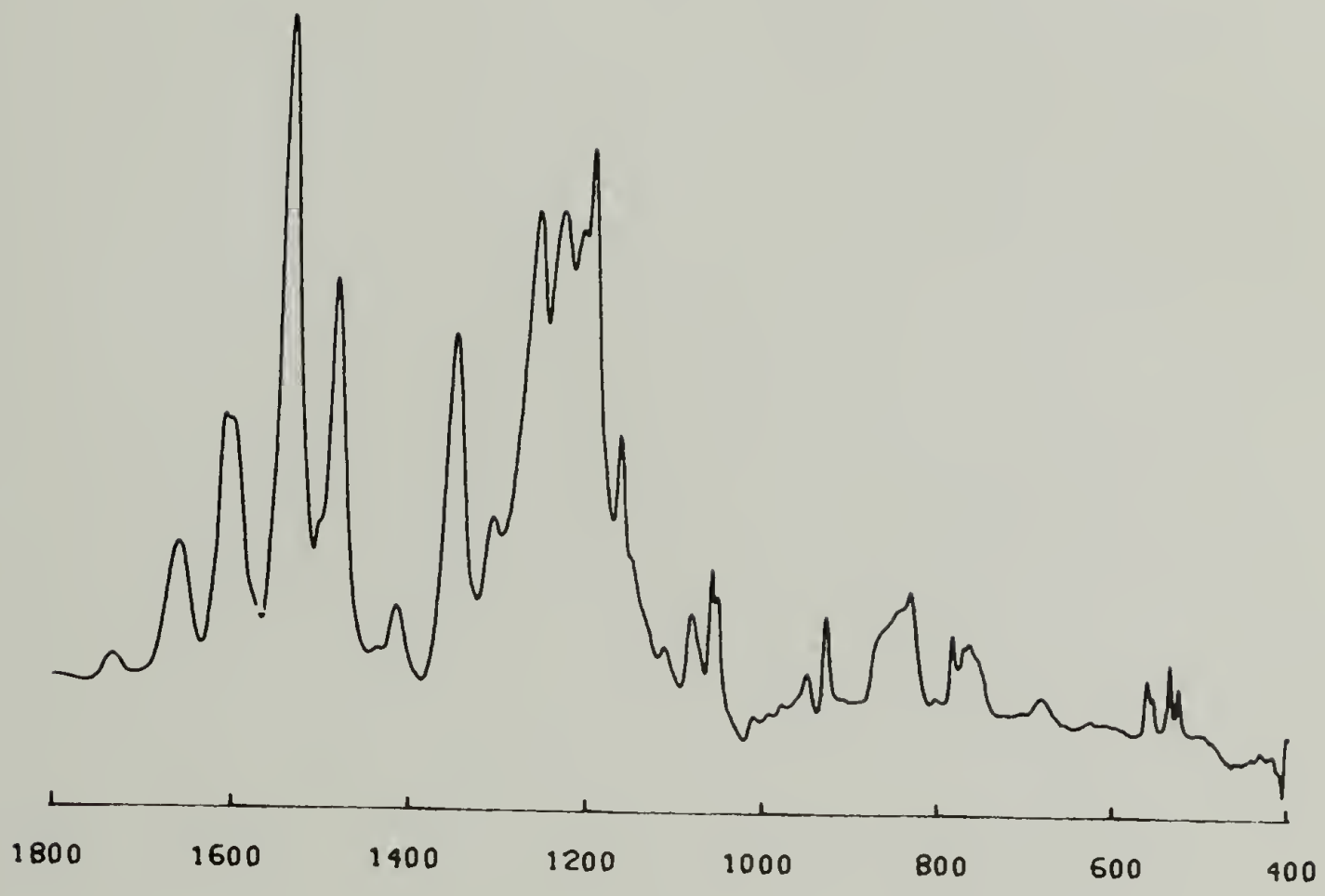

Figure 3.4. Fourier-transform infrared spectrum of nitrated PEEK (degree of nitration = 2.15).

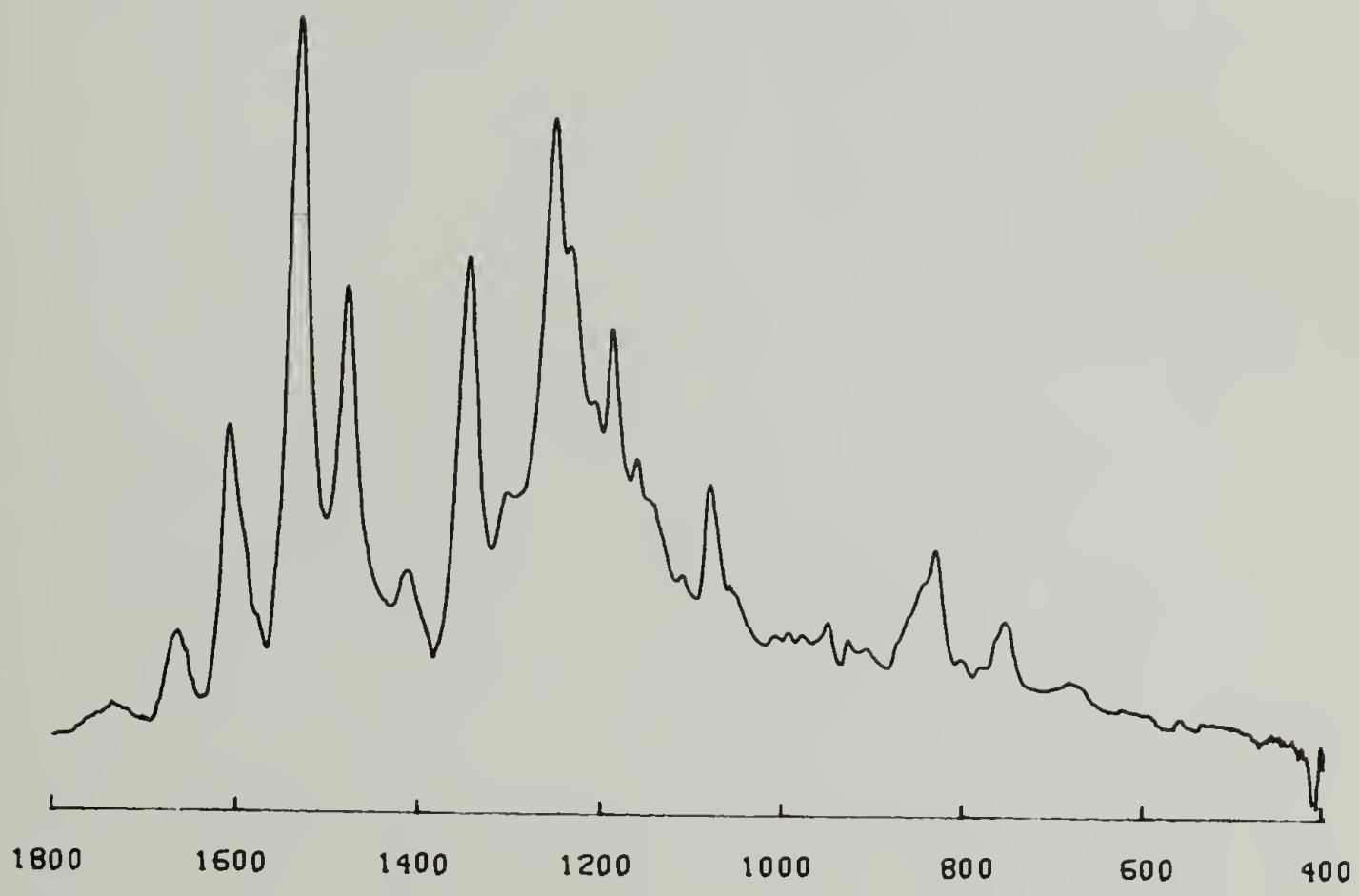

Figure 3.5. Fourier-transform infrared spectrum of nitrated PEEK (degree of nitration = 2.79).

assigned to the asymmetric and symmetric $-NO_2$ stretching modes, respectively. The intensities of these peaks varied proportionally with degree of nitration, when measured relative to the intensity of an absorption from a moity in the backbone (e.g., the carbonyl stretching band at 1665 cm^{-1}). Similar absorptions are found in other nitrated aromatics, such as nitrobenzene (1527 and 1348 cm^{-1}); frequency shifts for the NPEEKs compared to other nitrated species result from the presence of additional substituents (ether and carbonyl linkages) found in the polymers.

The absorption of the C-N stretching mode appeared at approximately 835 cm^{-1}. This band, which is strong in many nitroaromatics, was difficult to discern in the NPEEK spectra due to an overlapping absorption pattern from the aromatic C-H out-of-plane bending modes. Typical absorptions of this mode for two adjacent hydrogens (i.e., 1,4-disubstitution) are in the 800-850 cm^{-1} range (848 cm^{-1} in the parent PEEK spectrum (83)), and isolated hydrogen bending (i.e., 1,2,4-trisubstitution) are at slightly higher frequencies. The position and intensity of these bands are known to be highly sensitive to the nature and the electronegativity of the substituents (84). Thus, the decreasing intensity (with increasing degree of nitration) and possible shifting of the out-of-plane bending of two adjacent (5 and 6) hydrogens, the increasing intensity and position of a lone aromatic hydrogen out-of-plane bending and the increasing intensity of the C-N stretching would overlap and prevent definitive assignment.

An additional absorption which increased in intensity (relative to the 1665 cm^{-1} carbonyl peak) with increasing degree of nitration was observed at 1081 cm^{-1}, and was assigned to the in-plane C-H bending for an isolated hydrogen (1,2,4-trisubstitution). This absorption was not clearly observed in the spectra of sulfonated PEEK due to the presence of the symmetric $-SO_2-$ stretch observed at 1080 cm^{-1} (71). Conversely, the absorptions at 1162 and 1145 cm^{-1} decreased in intensity with increasing levels of nitration, and were assigned to the in-plane C-H bending for two adjacent hydrogens (1,4-disubstitution).

Two spectral changes were observed for absorptions associated with the ketone and ether moities. The peak at 1307 cm^{-1}, which has been described as a "motion of the carbonyl coupled with the rest of the molecule" (85), showed no measurable change over the parent PEEK for the spectra of the two lower degrees of nitration (X_N = 0.82 and 1.15), but increased sharply in relative intensity for the two more highly nitrated polymers (X_N = 2.15 and 2.79). As no changes in the positions of either band associated with the carbonyl (1665 and 1307 cm^{-1}) were observed for any of the nitrated polymers, the possibility of reaction of the ketone moity during nitration seems extremely unlikely. Thus, the change in intensity observed must result from changes in that portion of "the rest of the molecule" involved in the coupled motion, i.e., the phenylene rings adjacent to the ketone. Since no significant difference in the peak intensity was observed for X_N = 0.00 (parent PEEK), 0.82 and 1.15, but only for X_N = 2.15 and 2.79, it is likely that no change in the

benzophenone phenylene rings occurs until further reaction occurs, namely the nitration of these rings. It can be concluded that, for a polymer repeat unit, the initial nitration takes place on the phenylene ring adjacent to both ether linkages (the ring with the highest electron density, and thus, the most nucleophilic), with further nitration taking place on the two rings adjacent to the ketone (the rings with lower electron density). Steric considerations would indicate that nitro substitution on these rings is more probable at the sites meta to the ketone (ortho to the ether) than the sites ortho to the ketone.

The final significant difference observed in the NPEEK spectra was the change in the neat PEEK 1227 cm^{-1} absorption. This band was found initially to broaden ($X_N = 0.82$), and then to split into two separate absorptions at 1211 and 1237 cm^{-1}. Although the exact identity of this band in uncertain, it may result from a C-O ether vibration, a band which is known to be highly sensitive to ring substitution, especially with electrophilic subsituents (84).

In summary, the infrared spectra of the polymers conclusively demonstrate the presence of nitro groups. Nitration most probably occurs first on the phenylene rings with the greatest electron density (those between the two ether linkages) and then at those rings with lower electron density (those adjacent to the ketone linkage); the occurrence of multiple nitration of a ring cannot be clearly confirmed or excluded, but is thought to be only a remote possibility.

Several researchers have previously studied the carbon-13 NMR spectra of PEEK and a substituted (sulfonated) PEEK. Clark, et al (86,87) examined the solid-state carbon-13 spectrum of PEEK; their resonance assignments are given in Table 3.3.

Table 3.3 Assigned Carbon-13 Resonances of PEEK (86)

carbon	resonance (ppm)	position
1	192.8	carbonyl
2	132.3	oxy-1,4-phenylenecarbonyl ring carbonyl (ipso), ether (para)
3	132.3	oxy-1,4-phenylenecarbonyl ring carbonyl (ortho), ether (meta)
4	119.0	oxy-1,4-phenylenecarbonyl ring carbonyl (meta), ether (ortho)
5	150.8	oxy-1,4-phenylenecarbonyl ring carbonyl (para), ether (ipso)
6	159.8	oxy-1,4-phenyleneoxy ring ethers (ipso, para)
7	119.0	oxy-1,4-phenyleneoxy ring ethers (ortho, meta)

These values are in good agreement with predicted values with the exception of carbons 5 and 6 (the ether ipso carbons), for which the resonance assignments seem reversed. This reversal was confirmed by close examination of the spectra of two sulfonated PEEKs (71), which clearly show the resonance of carbon 5 to be about 9-11 ppm downfield from the resonance of carbon 6. Thus spectral calculation for nitrated PEEK were made based on the corrected assignments of PEEK.

The spectra of sulfonated PEEKs also give insight into changes due to substitution, and have applicability to the interpretation of an NPEEK spectrum. Although sulfonation was found to occur exclusively on the oxy-1,4-phenyleneoxy ring, changes in the resonances assigned to the oxy-1,4-phenylenecarbonyl rings (doublets) were observed. These would indicate the occurrence of long-range interactions with the $-SO_3H$ group. Also, the spectrum of one SPEEK ($X_S = 0.72$) showed 19 discernable resonances, compared to five for the parent polymer, and sulfonation occurs, at most, only once per polymer repeat unit!

The carbon-13 spectrum of nitrated PEEK ($X_N = 2.79$) in DMSO-d6 is shown in Figure 3.6. Close examination of the spectrum reveals the presence of over 50 separate and discernable resonances! A calculation of the number of theoretically possible resonances gave thirteen different resonances when accounting for only single ring substitution and 34 different values when disubstitution is permitted. If the possibility of ipso-substitution was included, a reaction often seen in aromatic nitration (88-90), the number of possible resonances became 17 and 45 for mono- and disubstitution, respectively. These numbers of theoretical resonances did not account for the existence of doublets which, at least in the case of sulfonation, may be 0.4 ppm apart. Thus, assignments of resonances in the NPEEK spectrum are extremely limited, and interpretation is, at best, only qualitative.

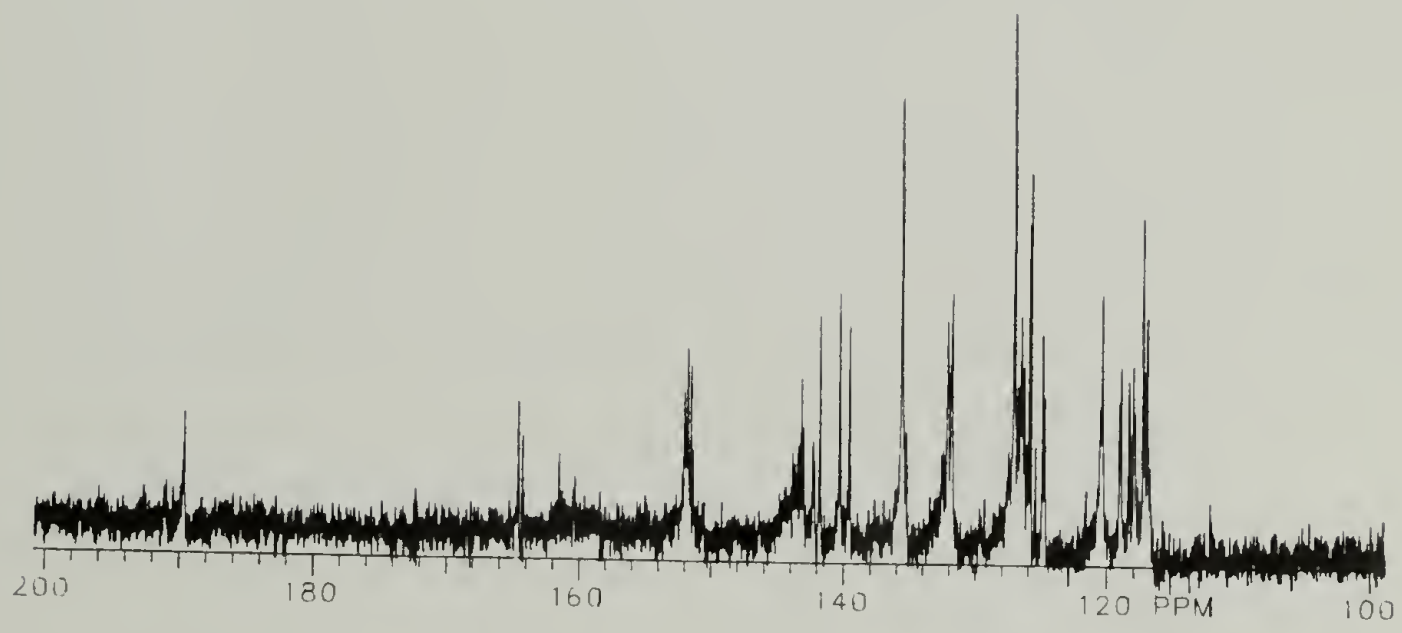

Figure 3.6. Carbon-13 NMR spectrum of nitrated PEEK (degree of nitration = 2.79).

The resonance at 189.8 ppm can clearly be assigned to the carbonyl carbon; this corresponds to values of 192.8 ppm in neat PEEK and 193.2 in SPEEK (X_S = 0.72). Shifting of this resonance in NPEEK might indicate nitration of the adjacent rings (as concluded from infrared spectra). Use of the intensity of this resonance as a standard for the other signals is not necessarily reliable due to the possibility of ipso-substitution at the adjacent phenylene ring position.

Three resonances are observed in the 160-165 ppm range (161.5, 164.3 and 164.6 ppm). Predicted resonance values indicate that only two carbons, regardless of substitution pattern, could possibly resonate in this range: the #3 and #5 carbons (see Table 3.3), both of which are on the ring adjacent to the carbonyl, and only when this same ring carries at least one nitro group. Since the resonance of #5 appears at 159.8 ppm in unmodified PEEK and at approximately 162 ppm in SPEEK, a possible assignment of the signals in the 160-165 ppm range might be to this #5 carbon, with no substitution on the oxy-1,4-phenylenecarbonyl rings, and a shifting and splitting on the resonance due to substitution on the oxy-1,4-phenyleneoxy ring. If this were the case, since the spectrum is for a polymer with Xn = 2.79, then trisubstitution of 79% (resulting in two resonances of equal intensity for carbon #5) and disubstitution of 21% (resulting in four resonances of two different intensities) of the oxy-1,4-phenyleneoxy ring would be required. As the nitration was performed in a dilute nitric acid/methanesulfonic acid solution at room temperature, the likelihood of any, let alone a significant degree, of

trisubstitution is very slight thermodynamically. Thus, subject to the stoichiometric ratio of the reactants, nitration is expected to occur at both the oxy-1,4-phenyleneoxy and the oxy-1,4-phenylenecarbonyl rings.

Ipso substitution is known to occur frequently in aromatic nitrations (88-90), and is a possible reaction in the nitration of PEEK. In this type of substitution, a nitro group replaces an existing substituent on the aromatic ring; in the case of PEEK, this would be an ether (substitution at carbons 5 and/or 6) or carbonyl (substitution at carbon 2) linkage, and would involve cleavage on the chain. Should this reaction occur in PEEK nitration, it would be expected to occur essentially exclusively at the carbonyl linkage since the resulting acylium ion is a more stable leaving group than the aroxy cation produced by cleavage of the ether. Also, ipso substitution has been observed to take place readily at the carbonyl in the nitrations of substituted acetophenone and benzophenone (91), was not observed at the ether linkage in the nitrations of various diaryl ethers except with fuming nitric acid at elevated temperatures (92a,b,c), and was observed to take place exclusively at the aldehyde in asarylaldehyde, rather than at any of the three methyl ether sites (93). Calculated resonance values indicate that the only possible signals in the 162-165 ppm range result from ipso substitution and cleavage at the carbonyl; two distinct resonances are observed in this range (164.3 and 164.6 ppm), confirming the occurrence of this type of substitution. The extent of ipso substitution could not be determined since the intensity of the carbonyl

carbon resonance, which might be used as a reference, would be diminished with increasing ipso nitration. A second confirmation for this substitution pattern is the appearance of a low-intensity signal at 173.5 ppm; this resonance can be assigned to the carboxylic carbon formed during the synthetic work-up from the acylium ion leaving group.

In order, the strongest resonances appeared at 127.0, 136.0, 125.8, 117.2 and 125.9 ppm. These signals were all within 2.0 ppm of theoretical values for six carbon atoms (seven substitution patterns), six carbons (four patterns), five carbons (seven patterns), eight carbons (five patterns) and five carbons (seven patterns), respectively, without accounting for potential doublet signals. This passel of possible patterns renders clear discernment of substitution patterns impossible.

There were no resonances which could clearly confirm the presence of more than the single nitration of any ring; the calculated resonance values for disubstitution were all too close to values obtained with single substitution to be distinguished experimentally. Should disubstitution occur on the oxy-1,4-phenyleneoxy ring, it is likely that the second nitro group would be meta to the first as nitro substituents are strongly meta-directing, and the ortho-directing effect of the two ethers offset. On the oxy-1,4-phenylenecarbonyl ring, it is likely that initial substitution on the #4 carbon is favored due to the combination of the ether ortho-direction and the carbonyl meta-direction, as well as steric interference of the ketone. Consequently, should additional

substitution take place, it would be expected on the other #4 carbon, which would be additionally activated by the meta-directing nitro. In the case of ipso nitration (carbon 2), additional substitution would be expected to occur at the #4 carbon, due to the combined ether ortho- and nirto meta-activation. As mentioned previously, trisubstitution is expected to be absent.

In summary, the carbon-13 NMR spectrum of the X_N = 2.79 polymer was found to be a very complicated spectrum, rendering definite assignment of resonances nearly impossible. The presence of signals in the 160-165 ppm range confirmed the nitration of the oxy-1,4-phenylenecarbonyl rings, a pattern not seen in the sulfonation of PEEK. Two of these resonances, at 164.3 and 164.6 ppm indicated the occurrence of ipso nitration, resulting in the cleaving of the polymer chain at the carbonyl. The occurrence of disubstitution on any ring could not be clearly confirmed or eliminated; trisubstitution was thought not to be present, given the relatively mild method of nitration.

All five nitrated PEEKs were determined to be completely amorphous and with glass transition temperatures of 156° C (X_N = 0.42), 157° C (0.82), 154° C (1.15), 141° C (2.15) and 138° C (2.79). These compare with a T_g of 149° C for the parent PEEK. The increase in T_g at lower nitration levels can be understood as resulting from a general hindering of rotation along the chain due to the presence of the moderately bulky nitro groups, similar to the increase seen with sulfonation. (Unlike

the $-SO_3H$ groups, however, the $-NO_2$ moities are not thought to be involved in any polar/ionic interactions.)

The decrease in T_g from a high of 157° C (X_N = 0.82) to 138° C (2.79) could result from either a general increase in free volume of the bulk polymer or from a decrease in molecular weight caused by a side reaction (such as ipso substitution) during nitration. (The former was observed for poly(p-phenylene terephthalates) (PpPT) when prepared using a nitrated monomer; the T_g of PpPT was reported as 267° C, while the polymer prepared from 2-nitroterephthalic acid had a T_g of 69° C (94,95).) Solution viscosity measurements of the three most highly nitrated polymers in nitrobenzene (considered to be a non-interacting solvent) yielded intrinsic viscosity values of 0.701, 0.250 and 0.133 dL/g for the X_N = 1.15, 2.15 and 2.79 polymers, respectively. The simultaneous decreases in glass transition temperatures and intrinsic viscosities indicated a decrease in average molecular weight. This independently confirmed the occurrence of ipso nitration.

Recalling that these three NPEEKs were soluble (at least to some extent) in several polar, nucleophilic solvents, cast samples of the X_N = 1.15, 2.15 and 2.79 polymers were examined by DSC for evidence of reaction with the solvent. Glass transition temperatures are given in Table 3.4. The values obtained from the cast polymers are in general agreement with the powder values with the exceptions of pyridine (X_N = 2.15, 2.79) and DMAc (2.79). In these cases, it is likely that a

further reaction takes place between the electrophilic polymer and the nucleophilic solvents.

Table 3.4 Glass Transition Temperatures for NPEEKs

	Degree of Nitration		
	1.15	2.15	2.79
Powder, as prepared	154	141	138
Cast samples:			
Nitrobenzene	158	142	141
M-cresol	158	-	-
Pyridine	154	134	132
DMAc	152	140	131
DMSO	-	141	131
DMF	-	144	139

The results of thermogravimetric analysis for PEEK (powder, as received) and the five NPEEKs are shown in Figures 3.7 - 3.12; a summary of the nitro group weight percent of the polymer, the onset temperatures of degradation and the "first step" weight losses are given in Table 3.5.

Comparisons of the nitrated polymers with PEEK indicated that nitration significantly decreases thermal stability, that thermal stability decreases with increasing levels of nitration and that unlike

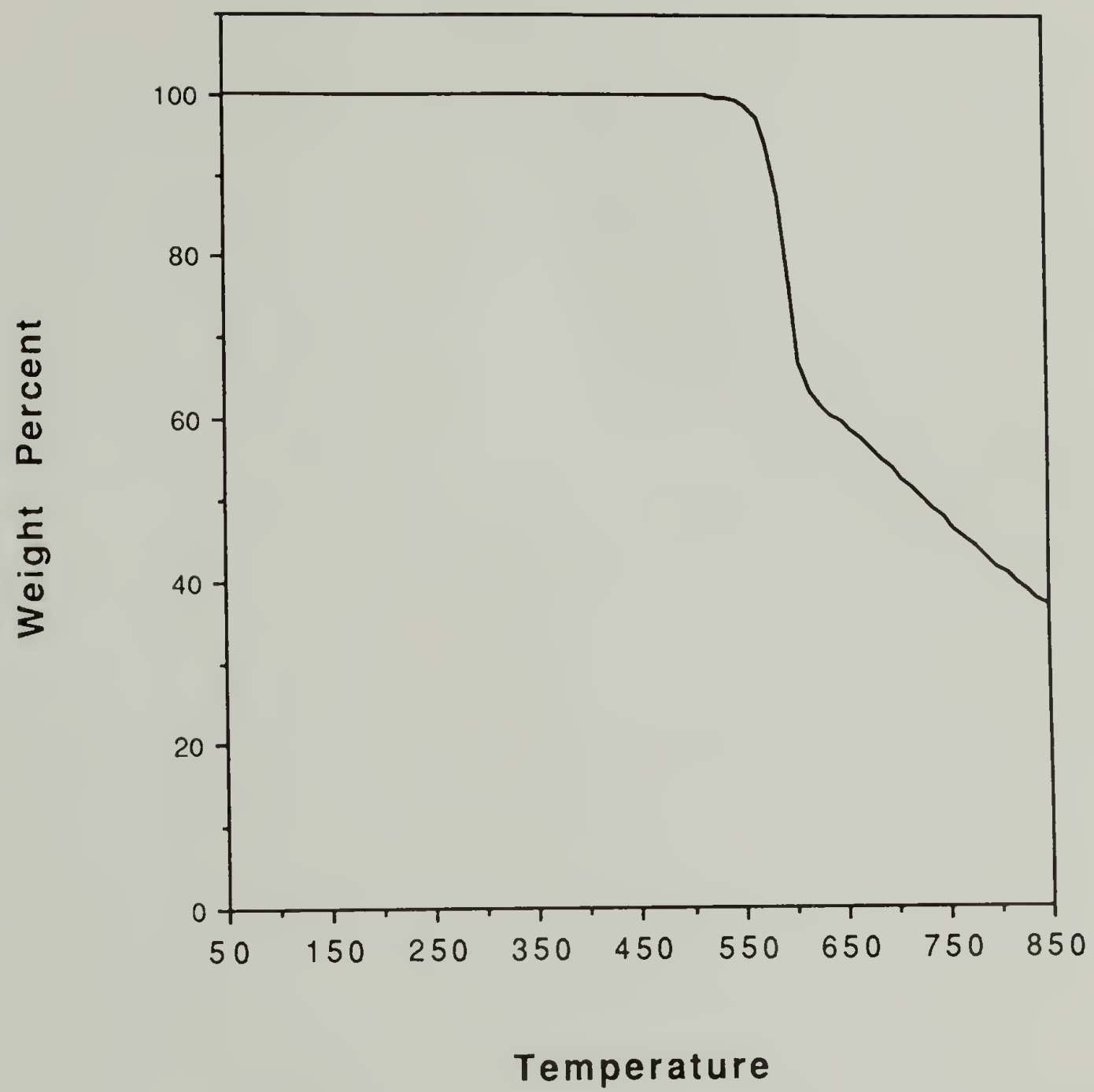

Figure 3.7. Thermogravimetric analysis of PEEK.

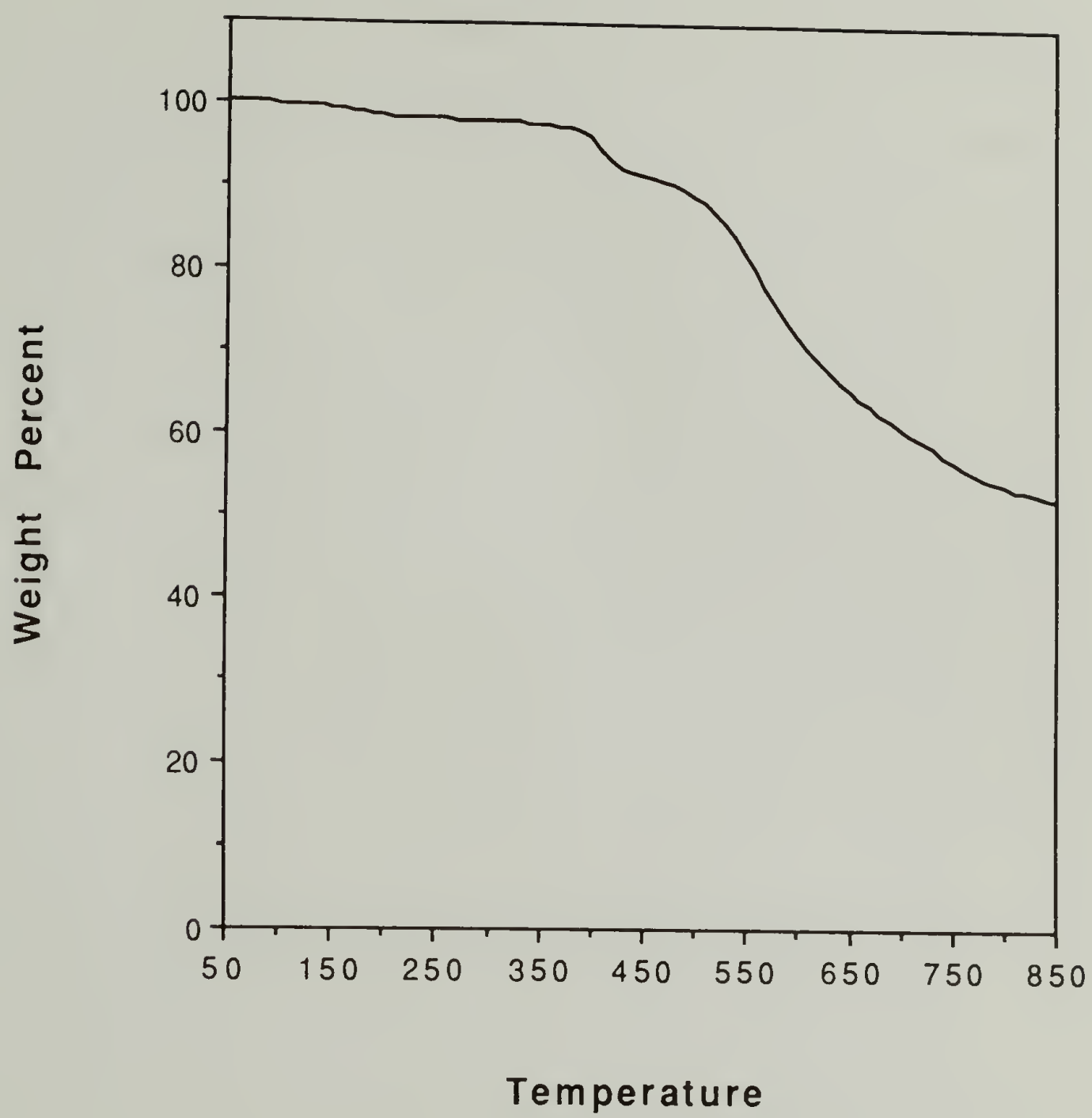

Figure 3.8. Thermogravimetric analysis of nitrated PEEK (degree of nitration = 0.42).

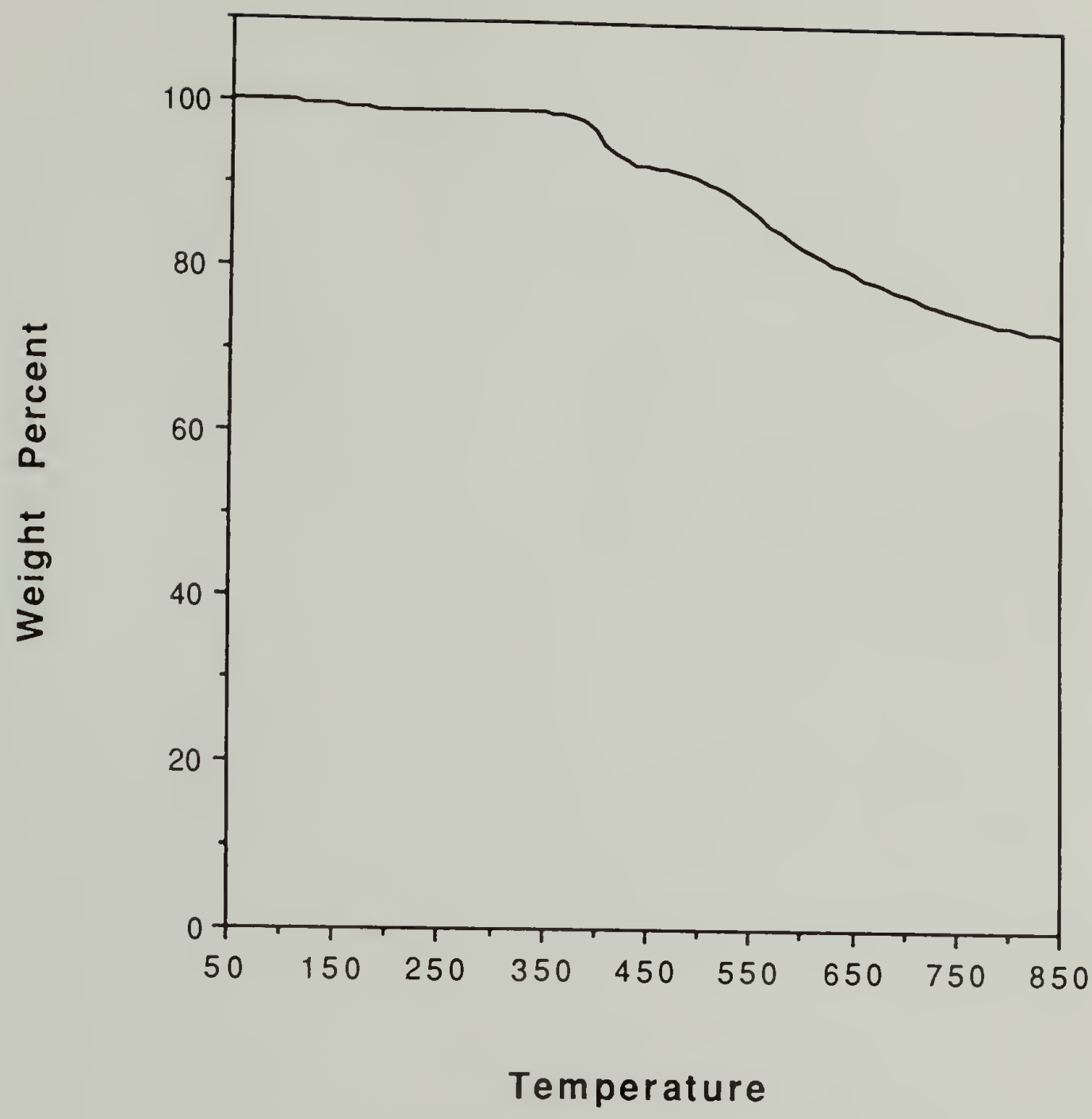

Figure 3.9. Thermogravimetric analysis of nitrated PEEK (degree of nitration = 0.82).

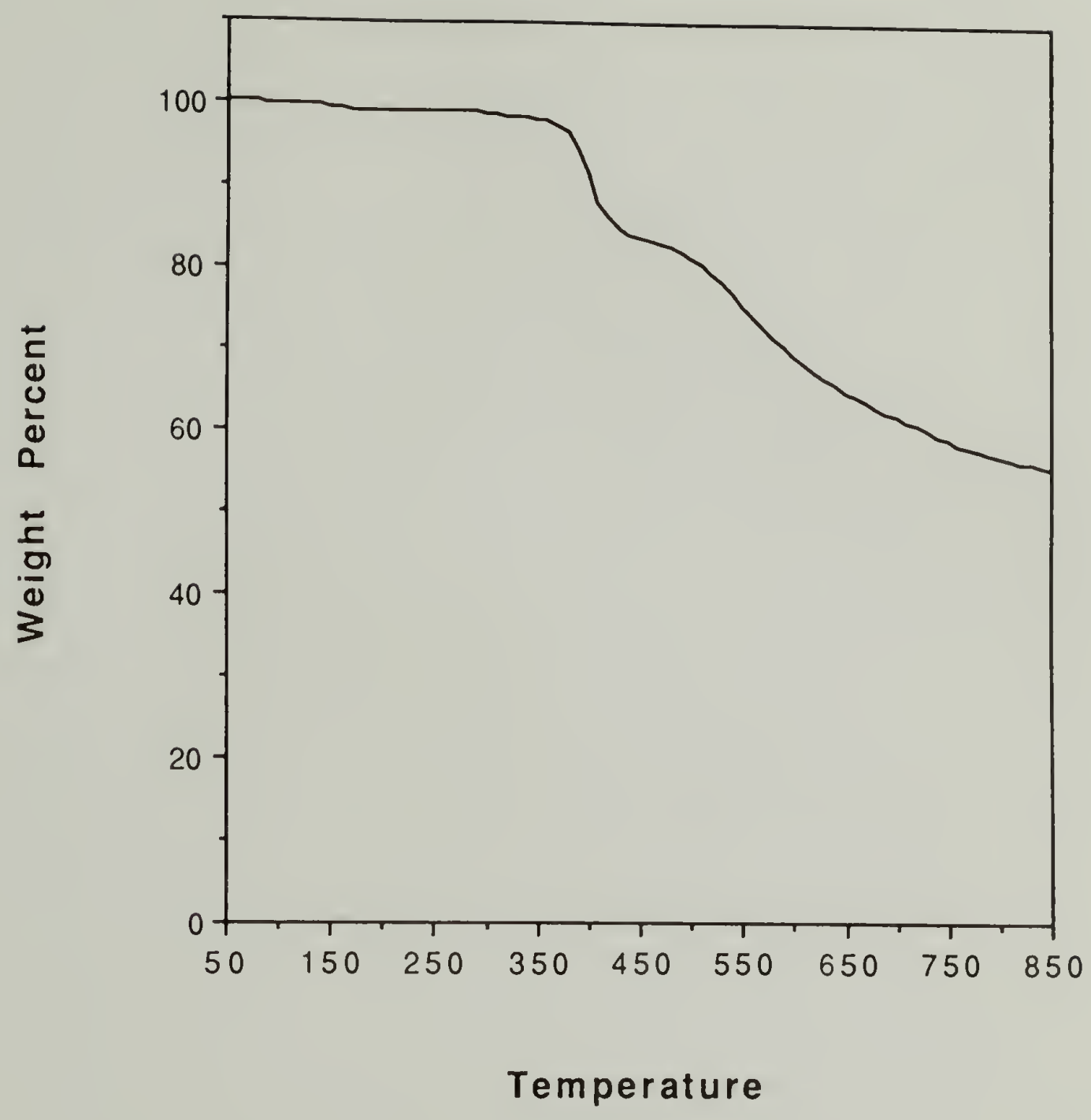

Figure 3.10. Thermogravimetric analysis of nitrated PEEK (degree of nitration = 1.15).

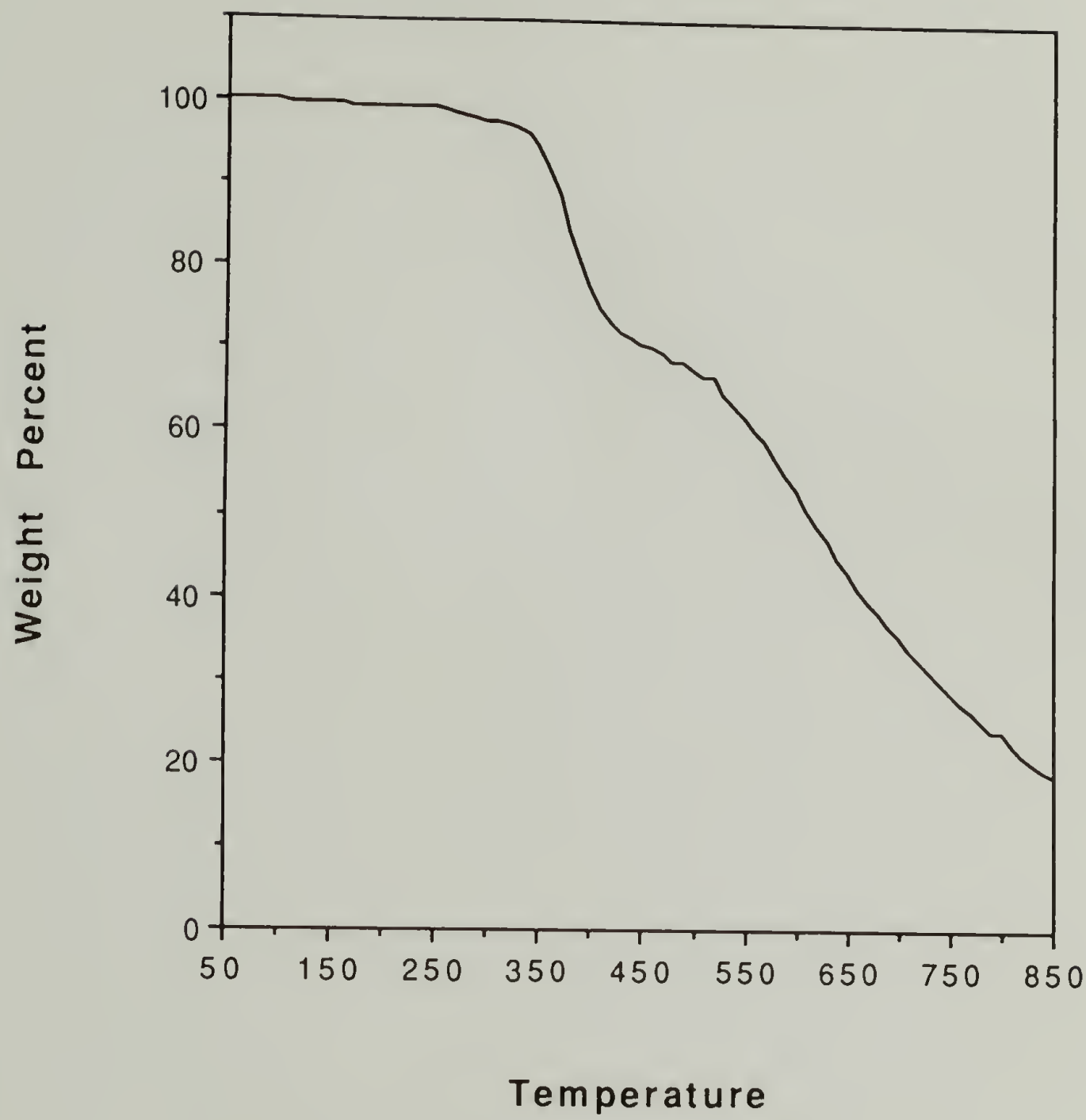

Figure 3.11. Thermogravimetric analysis of nitrated PEEK (degree of nitration = 2.15).

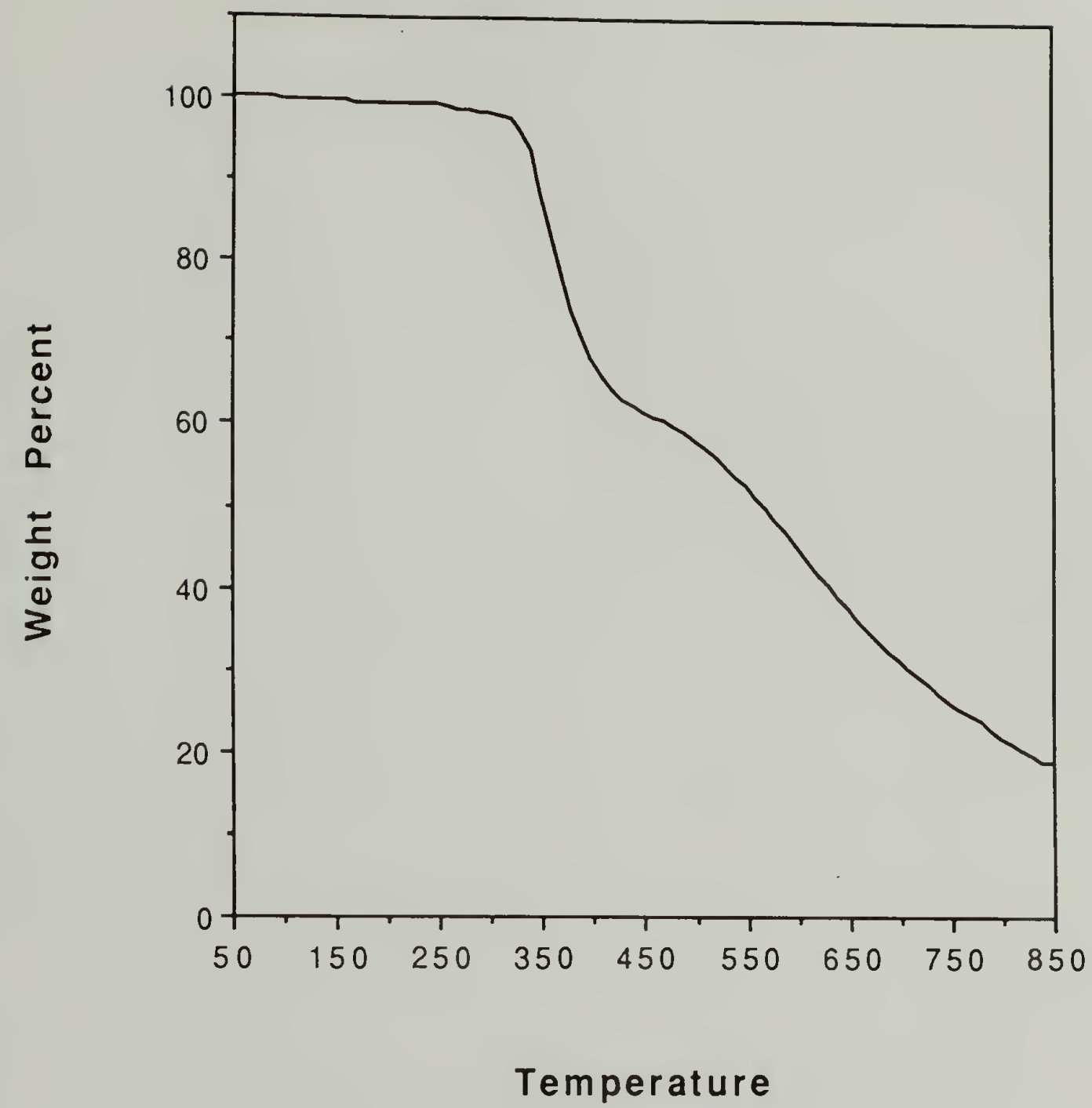

Figure 3.12. Thermogravimetric analysis of nitrated PEEK (degree of nitration = 2.79).

PEEK, thermal degradation of the NPEEKs occurred with two weight loss steps. The transition between these two steps occurred at approximately 420° C, independent of the degree of nitration.

Table 3.5 Thermogravimetry of PEEK and NPEEKs

X_N	Nitro wt. %	Onset temp. (°C)	"First step" wt. loss %
0.00	0.0	581	-
0.42	6.2	395	7.48
0.82	11.6	391	6.20
1.15	15.6	382	13.55
2.15	25.7	345	26.95
2.79	31.0	331	35.89

Because the fractional weight loss for the first step of degradation was close to the mass fraction of the nitro groups of each polymer, suggesting that this first step might be interpreted as the decomposition of the nitro groups, a partially degraded NPEEK (X_N = 2.79) sample was prepared by stopping decomposition at 450° C and was then subjected to elemental analysis. This study revealed that only 45.5% of the nitrogen was lost in this decomposition step, along with 21.0% of the carbon and just over 60% of the oxygen. Clearly, this first weight loss step was more complex than merely the loss of nitro groups and must include part of the polymer backbone. Mass spectroscopy of low molecular weight models (such as substituted benzophenones and

diphenyl ethers and also nitroaromatics) all yield carbon monoxide upon decomposition, either by ring fragmentation, or, in the case of the benzophenones, by elimination of the carbonyl. This latter process is known to be greatly enhanced by the presence of electron-withdrawing substituents (such as nitro groups) (96). The NPEEK oxygen weight loss corresponded to a loss through carbon monoxide (assuming all carbon is eliminated in this manner), nitric oxide and nitrogen dioxide (both are known to be eliminated from nitroaromatics, predominantly the latter). Thus, the first step weight loss cannot solely be ascribed to nitro decomposition; however, its correlation with the level of nitration may indicate the coincident occurrence of a decomposition mode activated by nitro substituents, e.g., elimination of the carbonyl moity as carbon dioxide.

3.1.4 Aminated PEEK

Three different procedures were studied for the reduction of nitrated PEEK to the corresponding amine: stannous chloride - hydrochloric acid, sodium polysulfide and zinc - acetic acid. The three "reduced" polymers were recovered as colored powders; the two former were pale orange, and the latter was off-white. Despite several washings, the third "reduced" polymer (zinc - acetic acid) still contained residual metal from synthesis (as determined by elemental analysis).

For the stannous chloride - hydrochloric acid and the sodium polysulfide "reduced" polymers, elemental analysis revealed no significant changes in the hydrogen/carbon ratio for either material compared to the parent NPEEK ($X_N = 0.82$). Also, the glass transition temperatures and the heat capacity changes at the glass transition for each of these materials were found to be not significantly different from that of the parent NPEEK. These results indicated that no clear reduction of the nitro groups was achieved by either of these two methods. No further analyses of these two materials were made.

Clear differences were observed in the case of the zinc - acetic acid reduced NPEEK: an increase in the hydrogen/carbon ratio was observed. This difference could not be taken as conclusive proof of reduction, however, as the degree of this change may have been skewed by the contribution of zinc hydroxide or zinc acetate impurities in the sample.

Definite confirmation of at least partial reduction from nitro to amine was found in the infrared spectrum of the reduced polymer. Although absorptions at 1535 and 1347 cm^{-1} were still present, two new peaks were found in the spectrum, when compared to that of the parent NPEEK (Figure 3.13), at approximately 2350 and 2325 cm^{-1}. Since very few moities absorb in this region, definite assignment of these peaks could be made; they indicate the presence of amine salts ($-NH_3^+$), which could only exist after reduction of nitro groups. (Exact positions of

such salts depend strongly on the nature of the moities involved; shifts of almost 200 cm^{-1} have been observed for a series of different anions.) In addition to these absorptions, amine salts generally show broad bands in the 1625-1500 and 1470-1310 cm^{-1} regions with exact positions again depending on the specific moities. The presence of these indescript bands in the vicinities of the two principal nitro group absorptions rendered the determination of the efficiency of the reduction reaction impossible.

The room temperature solubility of the aminated PEEK was found to be slightly different from the parent NPEEK; these results are given in Table 3.6. Several clear differences could be seen; one was that the solubility of APEEK in nitrobenzene was clearly less than for the parent NPEEK. This was expected since the structural differences between APEEK and nitrobenzene are greater than with NPEEK. A second definite difference was seen with formic acid. Since APEEK is a stronger base than NPEEK, it should be, and was, more soluble in an acid.

Results from DSC showed that APEEK is completely amorphous with a glass transition temperature of 161° C (compared to 157° C for the parent NPEEK). This slight increase in the T_g may result from more hindered rotations along the APEEK chain due to the presence of ionic interactions between the $-NH_3^+$ groups along the chain and the corresponding acetate anions.

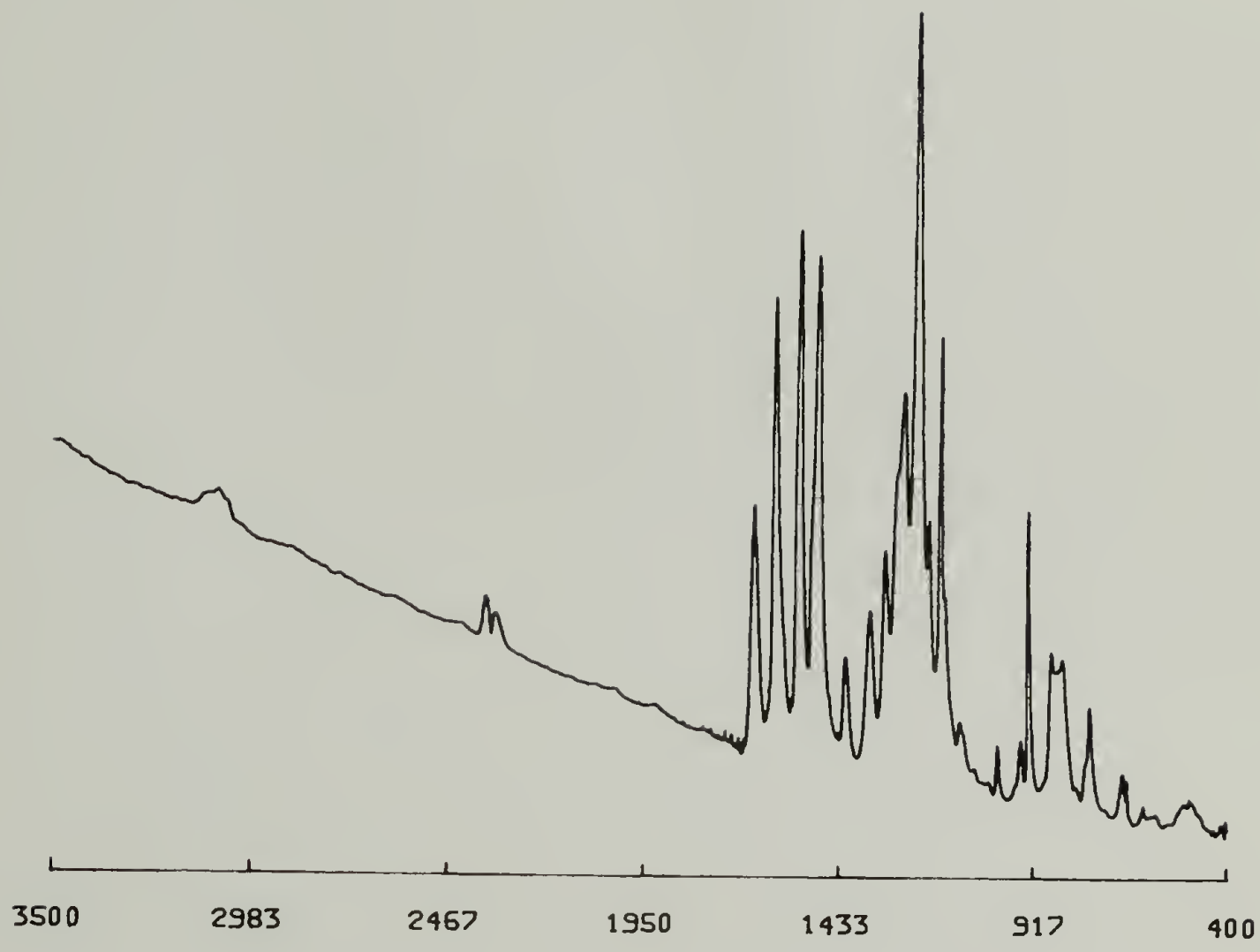

Figure 3.13 Fourier-transform infrared spectrum of aminated PEEK.

Table 3.6 Solubility of Aminated PEEK

solvent	APEEK	NPEEK (X_N = 0.82)
toluene	I	I
chloroform	PS	PS
chlorobenzene	I	I
acetone	I	I
nitrobenzene	SW	PS
m-cresol	S	PS
pyridine	PS	SW
dimethyl acetamide	PS	PS
dimethyl sulfoxide	PS	PS
dimethyl formamide	PS	I
benzyl alcohol	I	I
formic acid	PS	I
methanol	I	I
water	I	I

I = Insoluble
SW = Swollen
PS = Partially Soluble
S = Soluble

Thermogravimetric analysis showed the onset of degradation of APEEK to be at a much lower temperature (231° C) than any of the NPEEKs. The weight losses at various temperatures could not be accurately determined due to residual zinc in the polymer.

3.2 Blends

3.2.1 PEEK - Poly(amide imide)

The PEEK - poly(amide imide) blends were recovered in the form of grayish-brown powders, with no inhomogeneity visible to the naked eye. Analysis of the blends showed this pair of polymers to be immiscible; compositions with PAI weight fractions of 0.30 and higher possessed two distinct, sharp glass transitions at temperatures approximately equal in breadth and numerical value to those of the pure component polymers (Figure 3.14). Only one glass transition was observed for each of the other two blend compositions examined (PAI weight fractions of 0.10 and 0.20). The observation of single T_gs at these lower poly(amide imide) compositions several degrees higher than the T_g of pure PEEK may be interpreted as merely the inability to clearly discern the occurrence of a second, higher glass transition, the possibility of a very limited miscibility (perhaps of only the lower molecular weight PAI molecules with the PEEK), or as a combination of both factors.

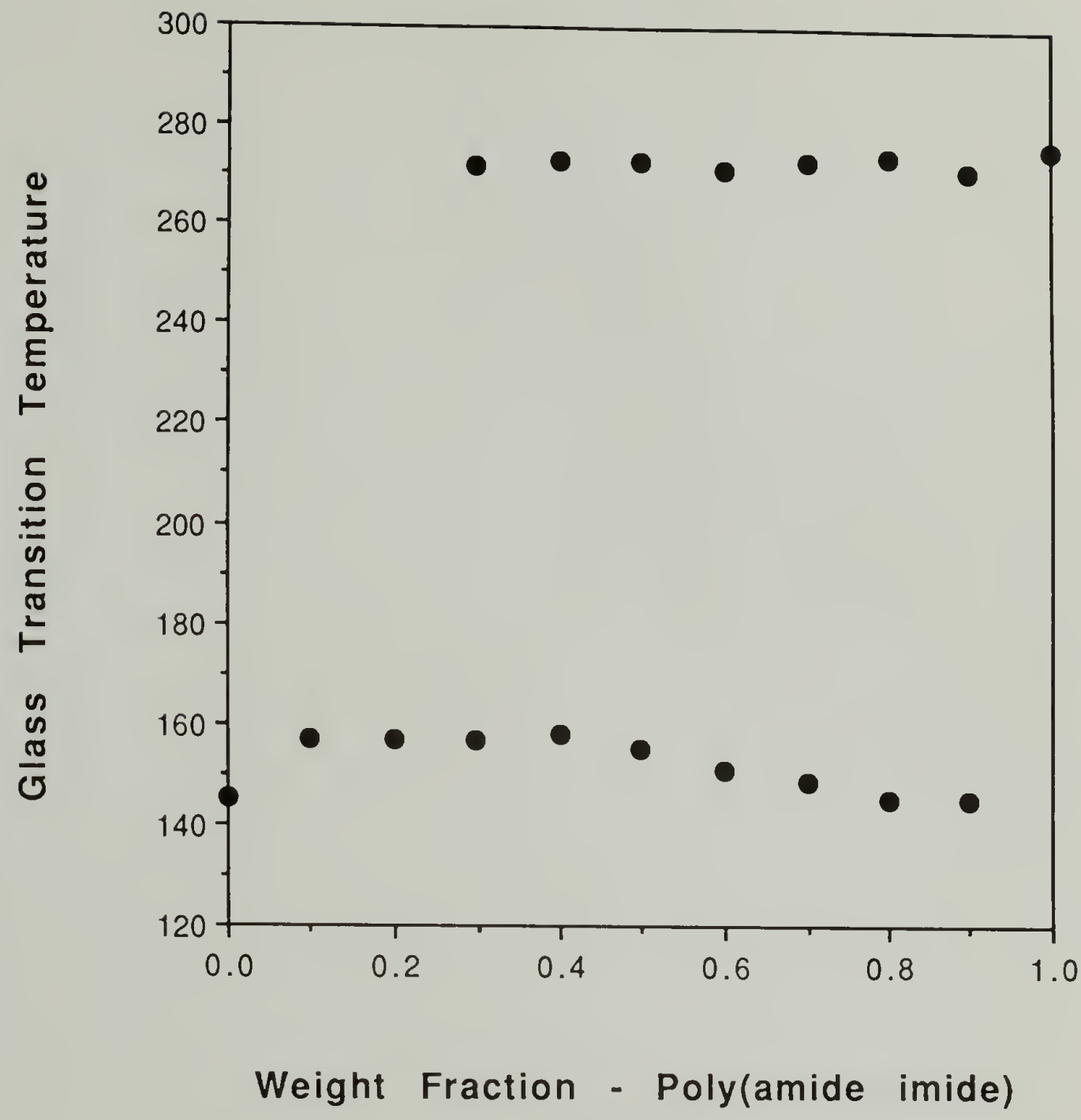

Figure 3.14. Glass transition temperatures of PEEK-PAI blends.

3.2.2 Poly(ether imide) - Poly(amide imide)

Cast films of the poly(ether imide) - poly(amide imide) blends were visibly cloudy. Analysis of the blends by DSC showed the existence of two glass transitions at temperatures approximately equal to those of the pure component polymers (Figure 3.15). The immiscibility of binary polyimide blends as seen here has also been observed with different polyimides (39,40).

3.2.3 Sulfonated PEEK - Polyimide

3.2.3.1 Binary

Cast films of the SPEEK-PEI and SPEEK-PAI blends were found to all be transparent, regardless of degree of sulfonation. The PEI blends were light amber in color, the PAI ones were darker. The color differences observed roughly correspond to the difference between the two original polyimides.

Results of the DSC analysis of the blends are shown in Figures 3.16-3.18 (PEI blends) and Figures 3.19-3.21 (PAI blends). For the SPEEK-PEI blends (all degrees of sulfonation), only a single T_g was observed for each composition. For the SPEEK (X_S = 0.42) blends, the difference in pure component T_gs was 36^0 C and for the X_S = 0.53 blends,

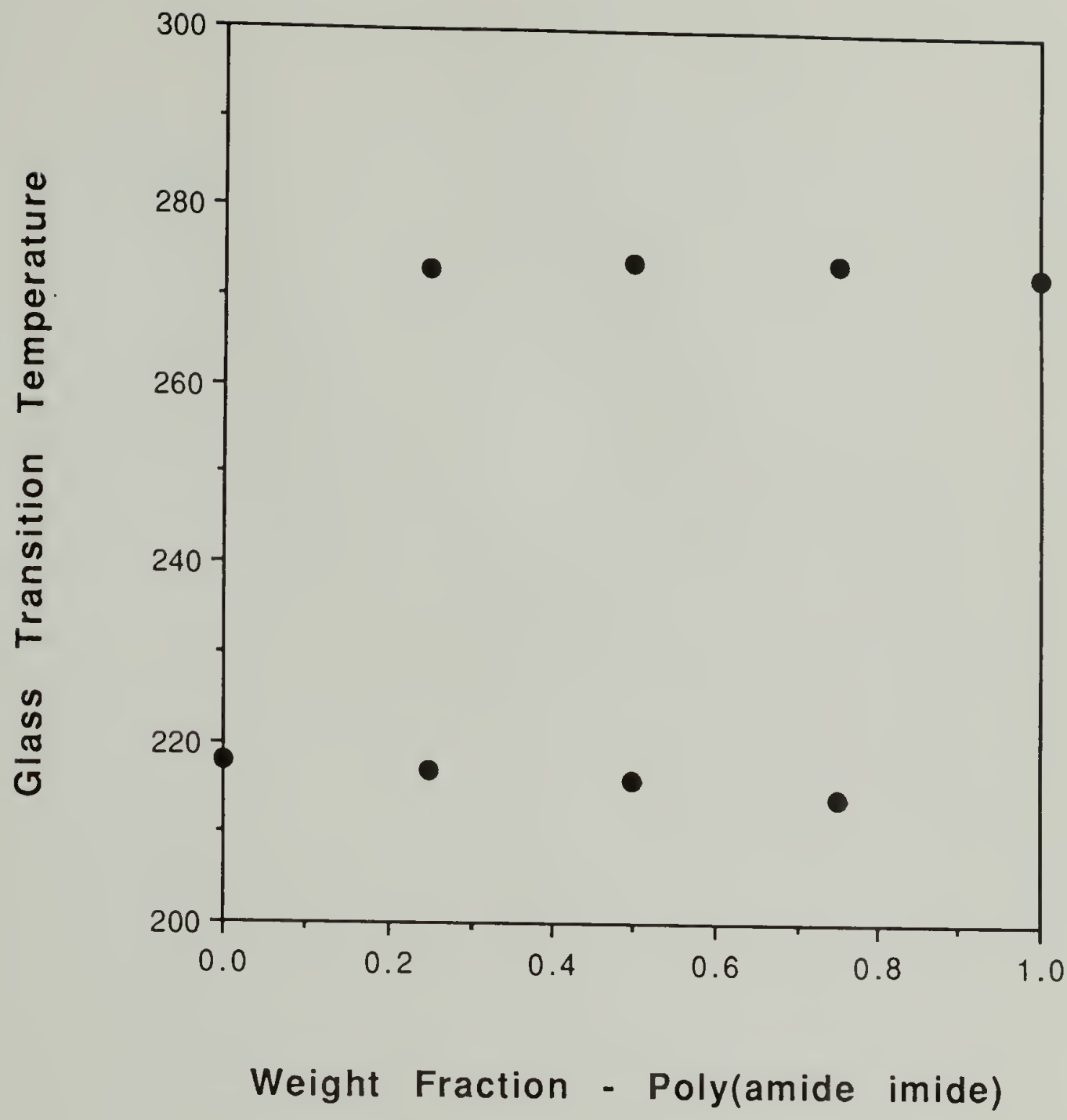

Figure 3.15. Glass transition temperatures of PEI-PAI blends.

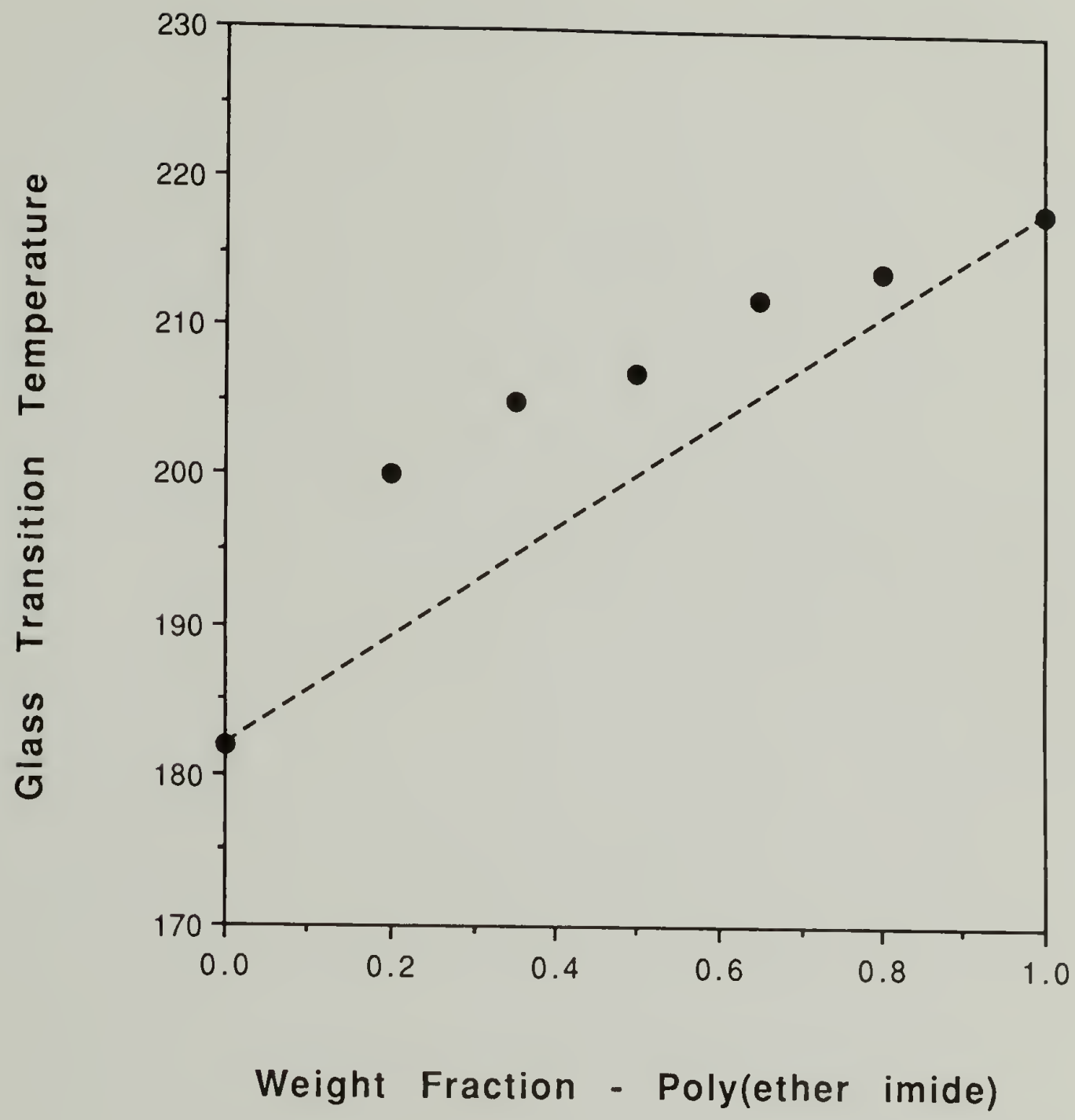

Figure 3.16. Glass transition temperatures for SPEEK-PEI blends (degree of sulfonation = 0.42).

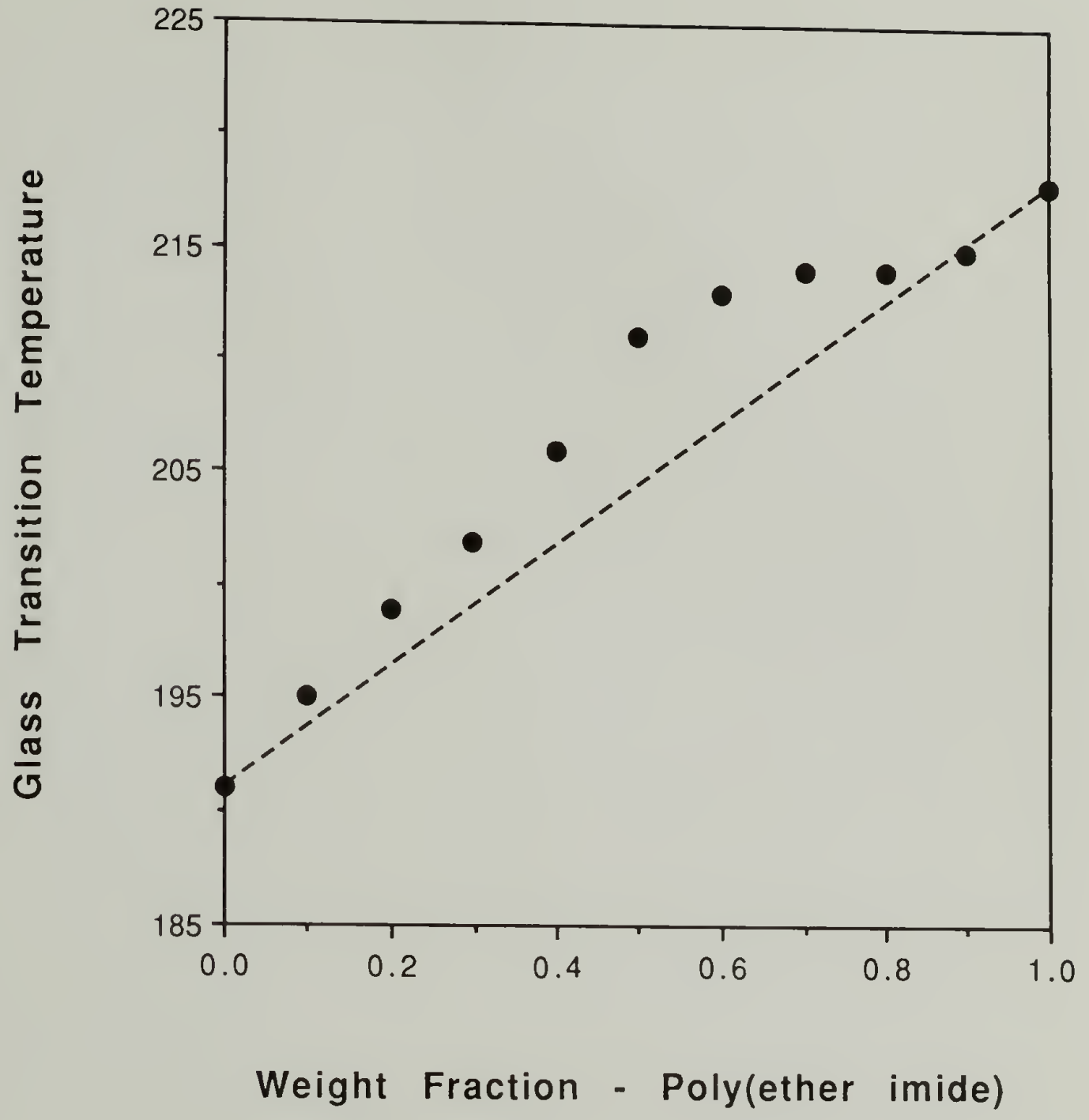

Figure 3.17. Glass transition temperatures for SPEEK-PEI blends (degree of sulfonation = 0.53).

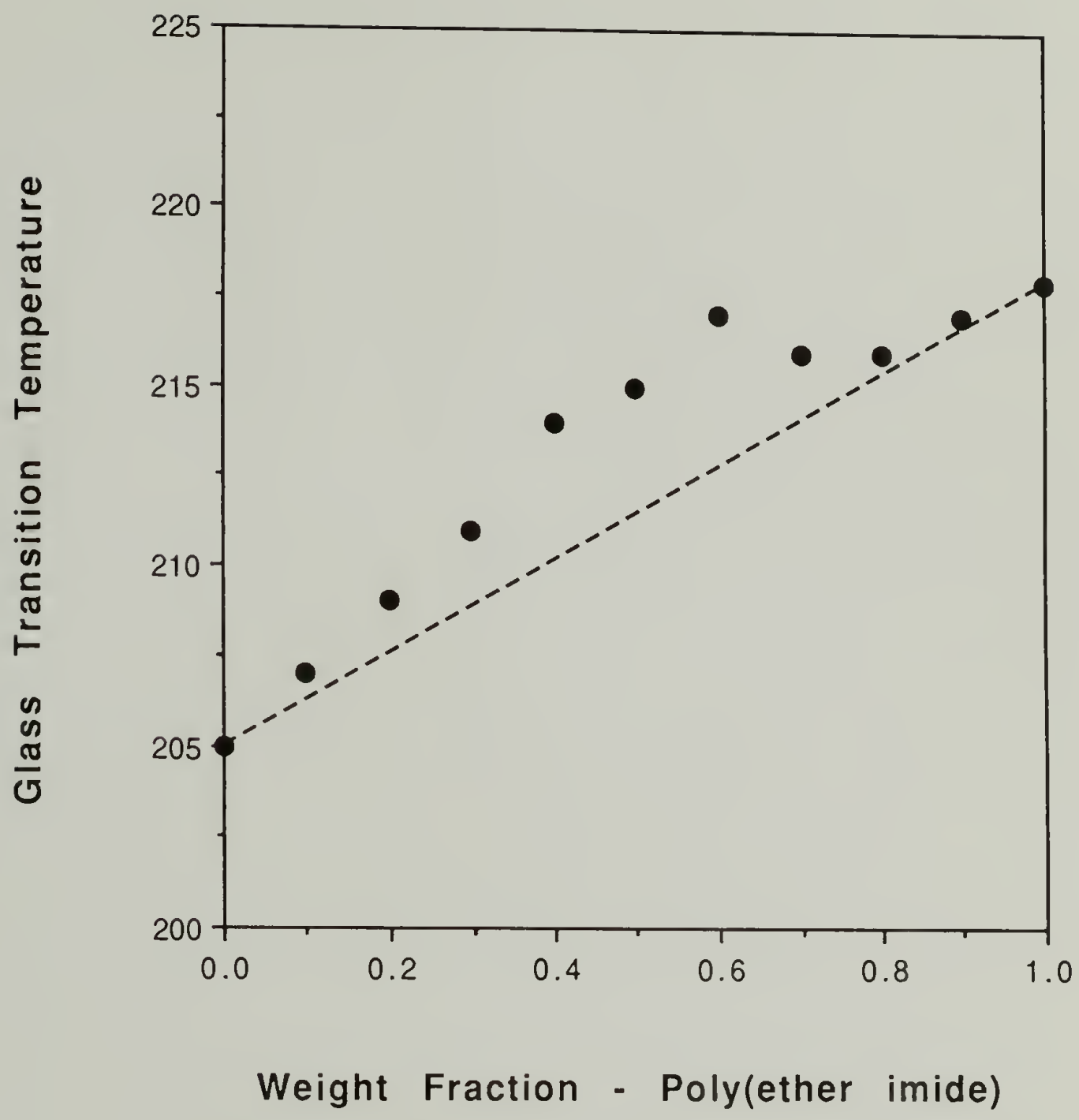

Figure 3.18. Glass transition temperatures for SPEEK-PEI blends (degree of sulfonation = 1.00).

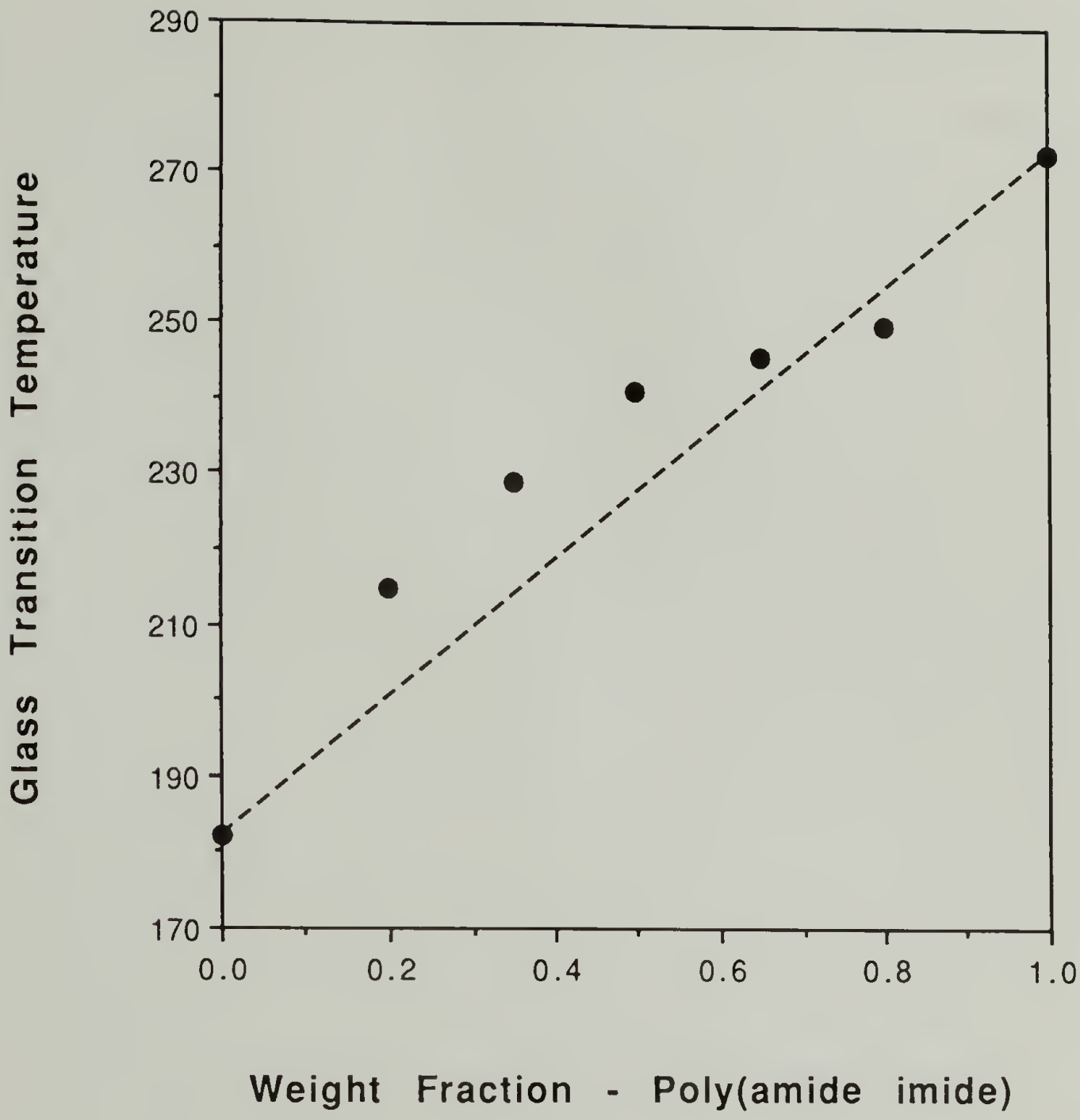

Figure 3.19. Glass transition temperatures for SPEEK-PAI blends (degree of sulfonation = 0.42).

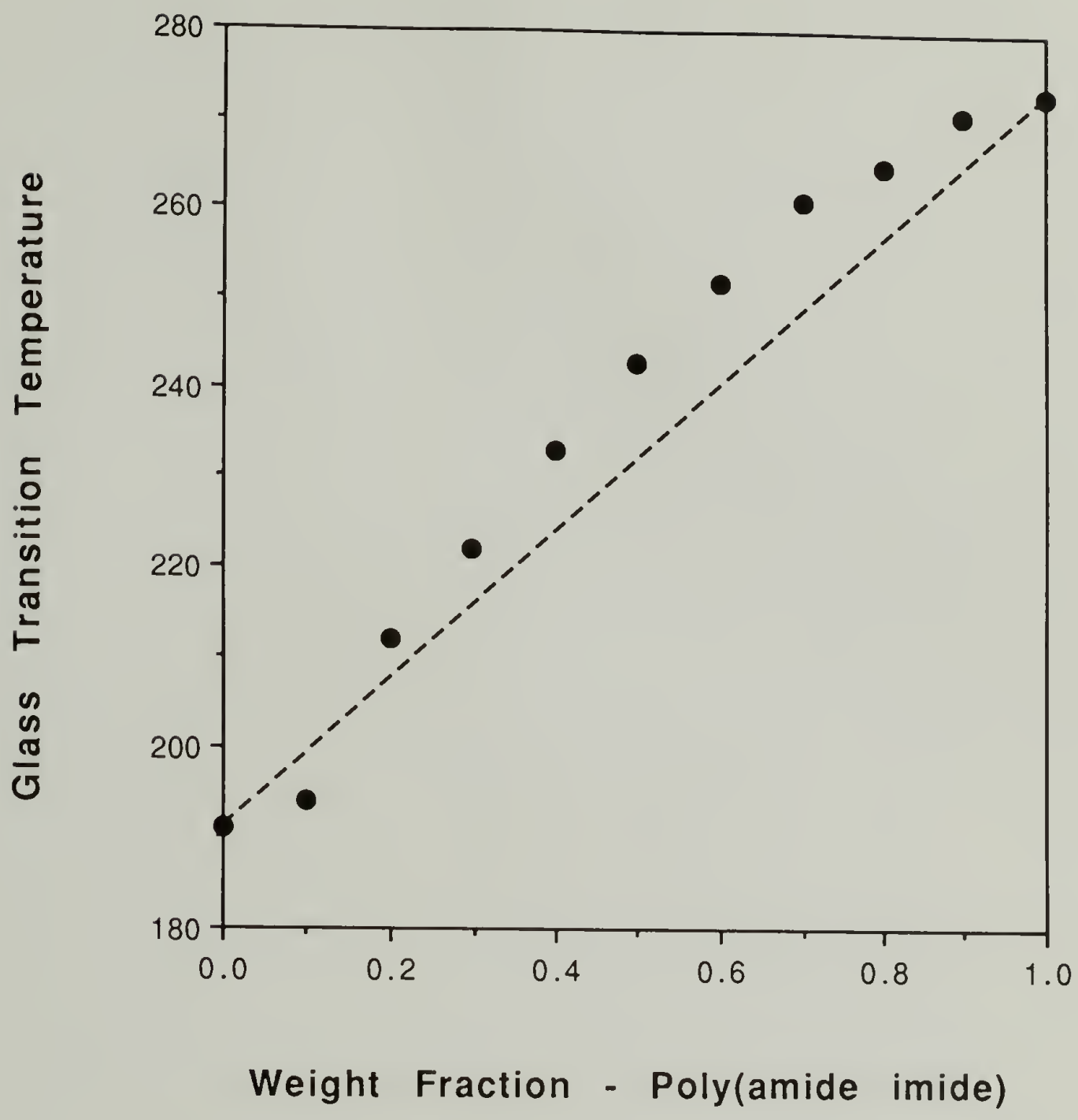

Figure 3.20. Glass transition temperatures for SPEEK-PAI blends (degree of sulfonation = 0.53).

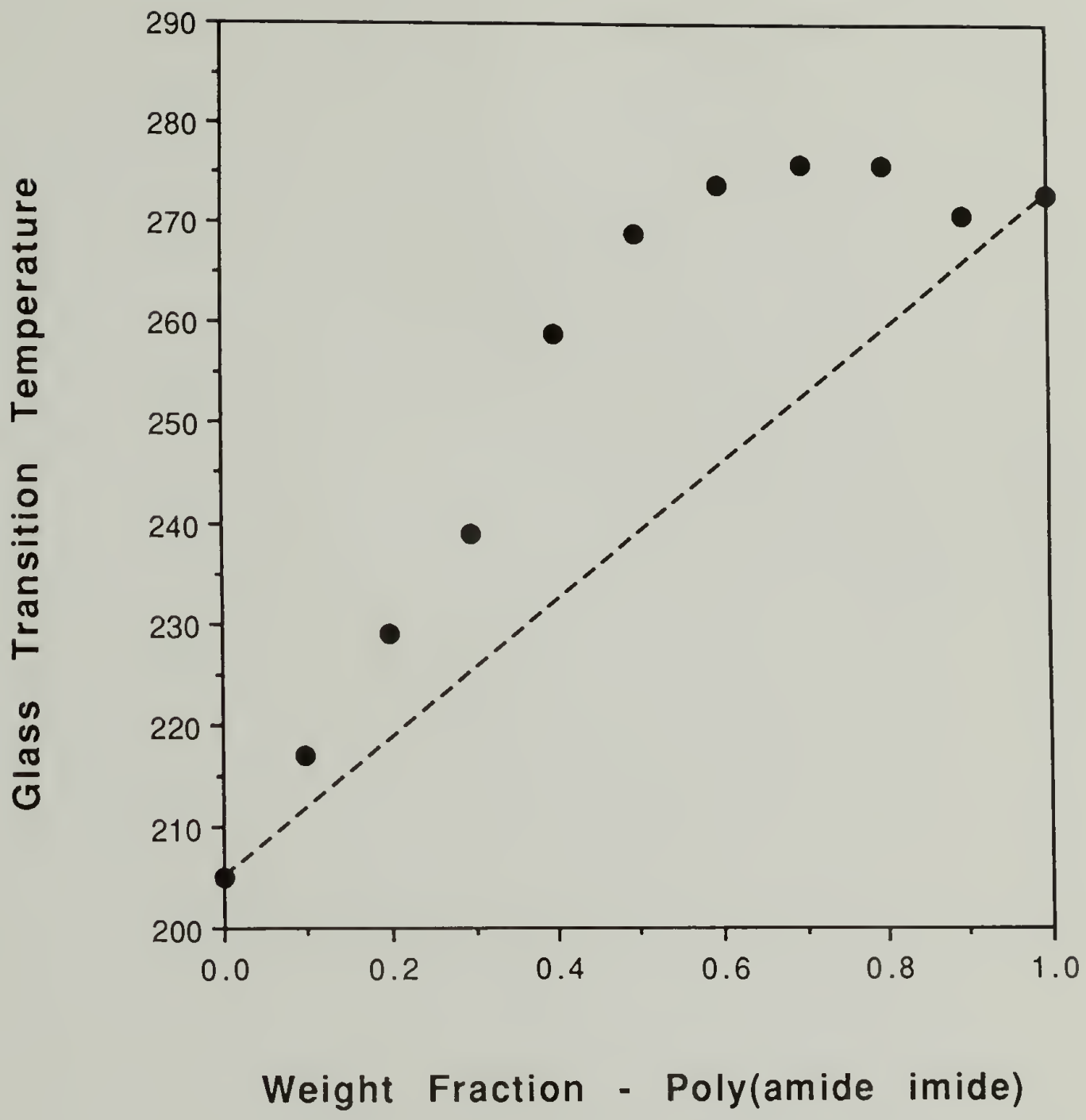

Figure 3.21. Glass transition temperatures for SPEEK-PAI blends (degree of sulfonation = 1.00).

27° C. The magnitude of these differences and the presence of single glass transitions for all studied compositions indicate complete miscibility. For the X_S = 1.00 blends, single glass transitions were observed, but, since the difference in the pure component T_gs in this system was only 13° C, the observation of single glass transitions did not conclusively indicate miscibility: two separate amorphous phases with different T_gs might be present, but the proximity of the glass transitions have made them indistinguishable. However, given that PEEK (non-sulfonated)-PEI blends (48) and the less sulfonated SPEEK-PEI blends were found to be miscible in all proportions, it was probable that the SPEEK (X_S = 1.00)-PEI blends are also miscible.

For the blends of each level of sulfonation, sharp T_gs were observed for blends with PEI weight fractions of $\geq$0.50, independent of degree of sulfonation. A slight broadening of the glass transitions was observed for those blends with PEI weight fractions <0.50. For compositions where broadening was observed, the extent of broadening was found to increase with increasing degree of sulfonation. This same trend was found to occur in the PEEK/SPEEK homopolymers.

For nearly all compositions and degrees of sulfonation, the experimentally determined T_gs were higher than the values expected from compositionally weighted averages. As non-sulfonated PEEK-PEI blends did not show this deviation but closely obeyed the Fox equation (48), these maximum deviations suggested the presence of strong intermolecular

interactions involving the sulfonic acid group and/or the sulfonated ring. The good agreement of the intrinsic viscosities of SPEEK (X_S = 0.53) samples before and after annealling and the complete DMAc solubility of 1:1 blend composition samples after annealling at 300° C for five minutes eliminated the possibility that the maximum deviations in Tg result from crosslinking.

For the SPEEK-PAI blends (all degrees of sulfonation), single, compositionally-dependent T_gs were observed. Since the minimum difference in pure component T_gs was 68° C (for X_S = 1.00), the blends could all clearly be termed as miscible in all proportions. In these blends, all the glass transitions were observed to be broader than for that of pure PAI; this broadening was found to increase slightly with both increasing weight fraction of SPEEK in the blends (for a given degree of sulfonation) and with degree of sulfonation (for a given composition). This was likely the result of local fluctuations in the strength of intermolecular interactions between the sulfonated PEEK and the poly(amide imide).

Since the SPEEK-PAI blend phase behavior changes from completely immiscible at X_S = 0.00 (i.e., the original PEEK) to completely miscible at X_S = 0.42, there must be a certain threshold level of sulfonation at which miscibility for all compositions is first achieved. Attempts to determine this threshold were thwarted by the difficulties encountered in blending the two polymers. The solubility of SPEEK in DMAc is

strongly dependent on the degree of sulfonation: the X_S = 0.53 polymer was soluble in DMAc at room temperature, the X_S = 0.42 polymer was soluble only in hot DMAc, and an X_S = 0.32 material was not soluble, but only swollen in this solvent (71). Thus, there was a lower limit on the degree of sulfonation possible for the preparation of SPEEK-PAI blends in DMAc solutions. Alternately, though the PEEK-PAI blends were prepared from mutual solutions of methanesulfonic acid (MSA), this solvent could not be used in preparing SPEEK-PAI blends. Sulfonation is a reversible reaction, with an equilibrium sulfonation level being affected by the acidity of the medium and the concentration of solvated SO3 (97), so that SPEEK would readily undergo desulfonation when dissolved in MSA. This placed an upper limit on the degree of sulfonation possible for preparation of blends in MSA, resulting in a gap in the sulfonation level which could not be studied. (Blending in the melt state was not possible due to the extremely limited quantities of sulfonated polymers.)

The glass transitions of the blends were again found to be generally higher than values predicted from simple weighted averages. As blend samples (equal SPEEK-PAI weight fractions) were found to be completely and readily soluble in DMAc at room temperature after annealling at 300° C for 5 minutes (and with the absence of change in SPEEK (X_S = 0.53) intrinsic viscosity with such annealling), the occurrence of these maximum deviations in the glass transition behavior

could not be attributed to crosslinking. Taken with the fact that PEEK-PAI blends have been found to be immiscible, these positive deviations suggested the presence of strong intermolecular interactions in the blends. The immiscibility of PEEK-PAI and the fact that the extent of these deviations varied with degree of sulfonation indicate that the sulfonic acid group and/or the sulfonated ring were directly involved in these specific interactions.

The strength of the intermolecular interactions found to occur in these blends strongly suggested that they were not merely dipolar in nature, but were one of three specific possibilities. The phase behavior observed could be caused either by hydrogen bonding between the sulfonic acid proton and a nucleophilic moity of the polyimides (e.g., the imide carbonyl), as was observed in blends of different polyimides with polybenzimidazole (43-45), by an acid-base interaction involving actual proton transfer from the sulfonic acid to a basic moity of the polyimide (e.g., the imide nitrogen), or by formation of an electron donor-acceptor complex between an electron-rich donor ring (e.g., the N-phenylenes of the polyimides) and an electron-poor acceptor ring (e.g., the sulfonated phenylenes).

Investigation into the nature of the specific interactions in the blends was carried out using Fourier-transform infrared (FTIR) and ultraviolet (UV) spectroscopy. Figure 3.22 shows the FTIR spectra of PAI, SPEEK (X_S = 0.53) and a 50/50 (w) blend of these two polymers

(bottom to top). The FTIR samples, cast onto KBr pellets, were prepared by the same procedure as those samples studied by thermal analysis. Close examination of the blend spectrum indicated it to be a compositionally weighted addition of the pure component spectra. As changes in the phthalimide carbonyl bands were observed in the case of known hydrogen bonding (43-46), further analysis of these bands was performed. The symmetric and asymmetric stretches of the PAI imide carbonyls were found to occur at 1780 and 1724 cm^{-1}, respectively; the former was of much lower intensity than the latter. For the symmetric stretching band, no measurable differences, either in position, shape (peak symmetry) or breadth (full width at half height, FWHH) were observed. For the stronger, asymmetric stretching band, changes were very minor. The band position moved from 1724 to 1725 cm^{-1} upon blending (spectral resolution was 2 cm^{-1}), the FWHH changed from a pure component value of 27 cm^{-1} to 24 cm^{-1} for the blend, and no change in peak symmetry was observed. Thus, no conclusive evidence for hydrogen bonding was found in the PAI-SPEEK blends.

Changes in the infrared region would also be expected with the presence of an acid-base interaction, especially in the bands associated with the sulfonic acid group. These bands have been identified as a broad band at 3450-3430 cm^{-1} (O-H vibration), and sharp bands at 1252 cm^{-1} (asymmetric O=S=O stretch), 1080 cm^{-1} (symmetric O=S=O) stretch), 1024 cm^{-1} (S=O stretch) and 709 cm^{-1} (S-O stretch) (71). These bands were all observed in both the pure SPEEK and in the blend spectra.

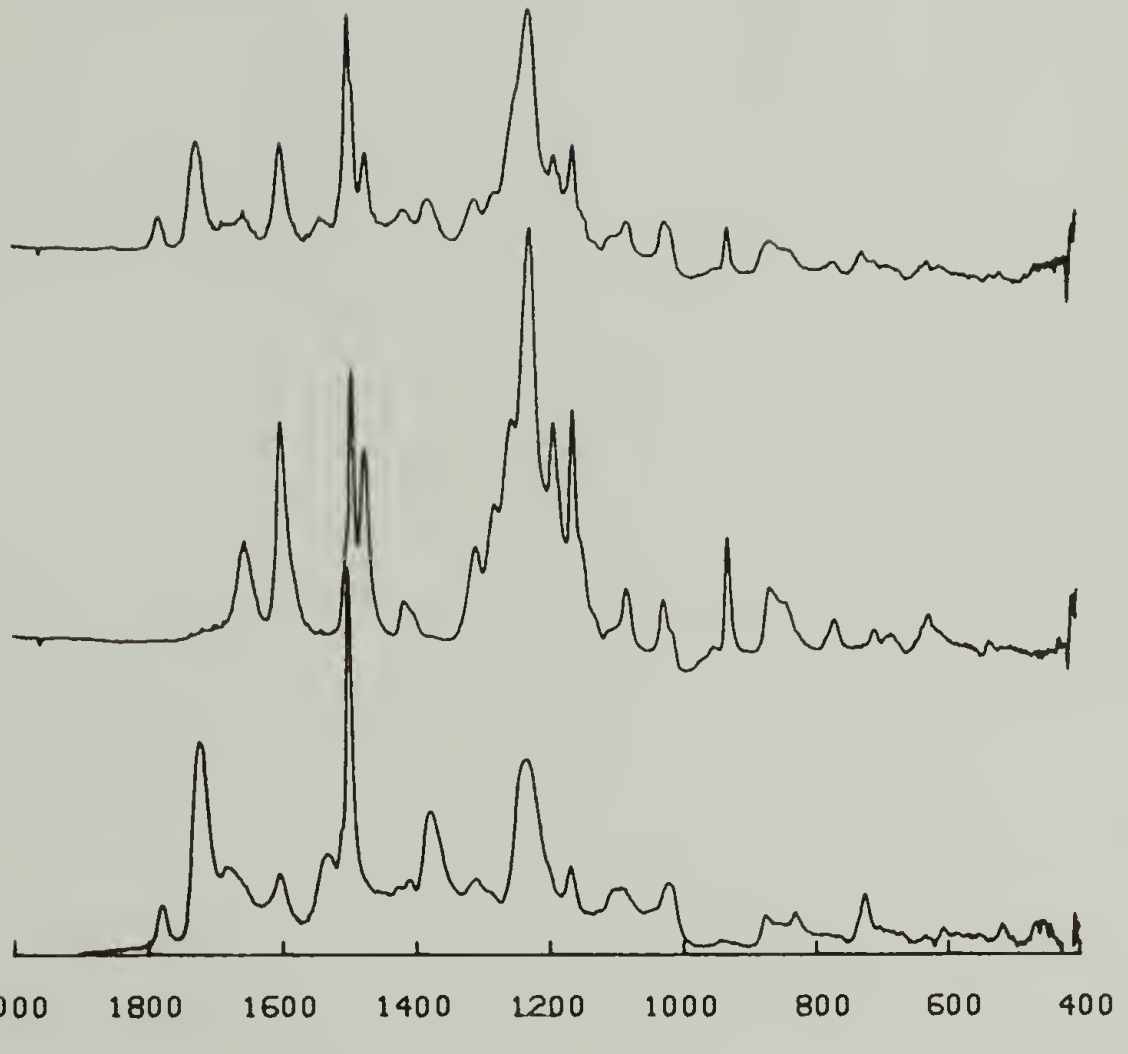

Figure 3.22. Fourier-transform infrared spectra of PAI, sulfonated PEEK (degree of sulfonation = 0.53) and a 50/50 (w) blend.

No changes in the sulfur-oxygen peak positions or relative intensities were found; the diffusiveness of the O-H vibration at 3450-3430 cm^{-1} limited its complete analysis. Again, the absence of changes upon blending indicated that there was no conclusive evidence for an acid-base interaction in the PAI-SPEEK system.

The third possible, and typically least understood, intermolecular interaction which might be responsible for the phase behavior was formation of electron donor-acceptor (EDA) complexes between the sulfonated rings of SPEEK and the N-phenylene rings of the polyimides. This type of complex, which is formed by delocalization of an electron between electron-rich and electrophilic moities, is occasionally referred to as a charge-transfer complex (CTC), especially if complete electron transfer is involved. Evidence of this kind of interaction would be found primarily in the ultraviolet and/or visible spectra, and would evidenced by a blend spectra which strongly deviated from Beer's law. These deviations might appear either as new peaks or as greatly increased absorptions across a wavelength band. The spectral position and intensity of EDA complexes are functions of the ionization potential of the donor and the electronic affinity of the acceptor; several authors discuss the nature of EDA complexes in greater detail (98-101).

Ultraviolet spectra for SPEEK (X_S = 0.53 and 1.00), PAI and equal weight fraction blends are shown in Figures 3.22 and 3.23. (Spectra for the SPEEK (0.42) polymer and its blends could not be obtained due to the

limited solubility of that polymer at room temperature.) The absorbtivity of the SPEEK (0.53) blend was found to be greater than the sum of the component absorbtivities for all wavelengths in the region studied; this deviation, or "excess" absorption, was at least ten percent (at 293 nm) and as much as thirty-four percent (at 256 and 315 nm) greater in the blend spectrum, depending on the particular wavelength. Two regions were found with the greatest absorbtivity differences. The range of 250-267 nm was bimodal, with local maxima at 252 nm (blend absorbtivity was 31.0% greater than the sum of the components) and 264 nm (32.7% greater), and a local minimum at 255 nm (19% greater); the second range was at 311-315 nm, with a maximum at 315 nm (34.1% greater than the component sum). The absorbtivity of the SPEEK (1.00) blend was found to also be greater at all wavelengths than the sum of the component spectra, with the "excess" absorbtivity being at least 6.4 and as much as 60.3% greater in the range studied. Again, two regions were found with the largest absorbtivity differences: a bimodal region at 251-270 nm having local maxima at 256 nm (18% greater) and 266 nm (40.2% greater) and a minimum at 257 nm (13.5%), and a second region at 304-315 nm, with a maximum at 315 nm (60.3% greater than the component sum).

The UV spectra for the SPEEK (1.00), PEI and their equal weight fraction blends are shown in Figure 3.25. The absorbtivity of the blend was found to be 6.9 to 17.0% greater than the sum of the component absorbtivities in the region examined. One regime was found to possess

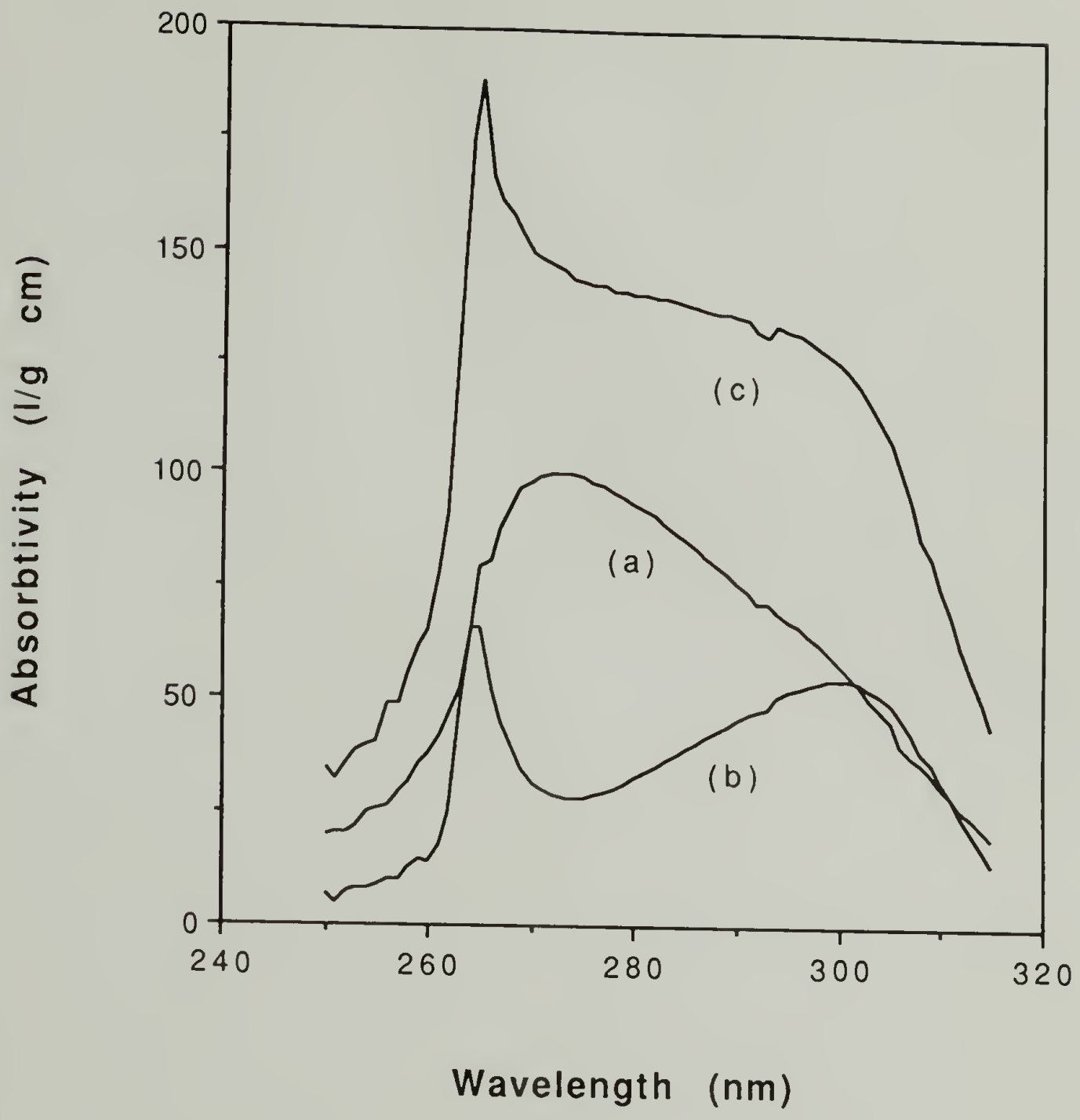

Figure 3.23. Ultraviolet spectra of PAI (a), sulfonated PEEK (b) (degree of sulfonation = 0.53) and a 50/50 (w) blend (c).

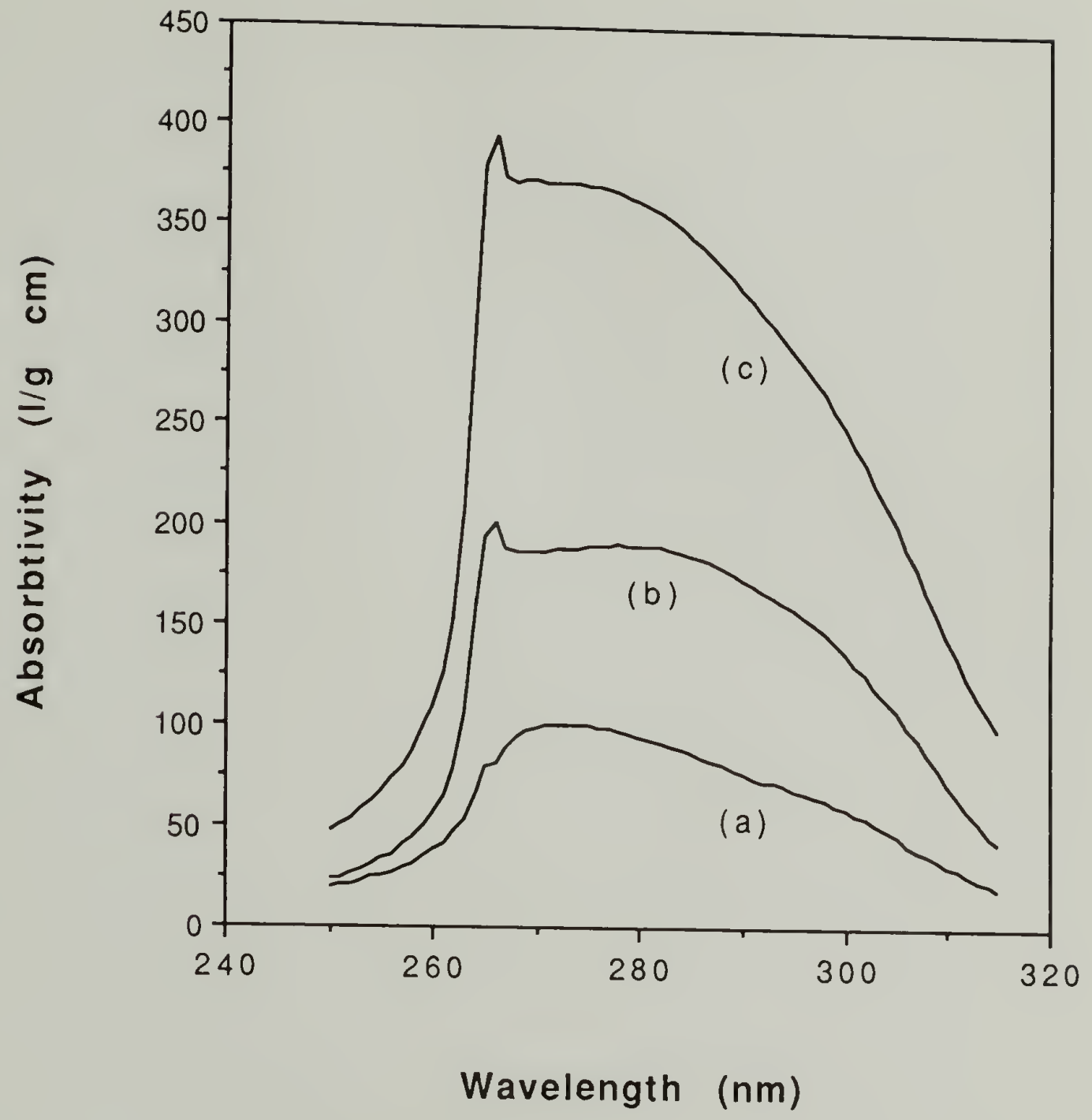

Figure 3.24. Ultraviolet spectra of PAI (a), sulfonated PEEK (b) (degree of sulfonation = 1.00) and a 50/50 (w) blend (c).

a large "excess" absorption, namely the 253-263 nm region. This band had a maximum at 254 nm, with an absorbtivity 17.0% greater than the sum of the component spectra. (The spectrum of the SPEEK (0.53)-PEI blend was also examined. Although a similar "excess" absorption pattern was observed, it was never greater than ten percent at any wavelength, and was only 2-3% greater at most wavelengths. This small difference between the blend and the summed component spectra rendered accurate analysis meaningless.)

A comparison of the spectra of the various blends gave greater insight into the nature of the EDA complexes observed. The spectra for the two PAI blends both showed two similar regions of large "excess" absorption (the lower, bimodal): 250-267 nm and 311-315 nm for the SPEEK (0.53) blend and 251-270 nm and 304-315 nm for the X_S = 1.00 blend. The local maxima in each of these ranges also were in good agreement: 252, 264 and 315 nm (0.53) and 256, 266 and 315 nm (1.00). This was to be expected since the positions of spectral maxima depend principally on the ionization potential of the electron donor; for PAI, these donor moities are the N-phenylenes from the m-phenylenediamine and 4,4'-oxydianiline reagents. The degree of "excess" absorption in the blends, like the positive deviations in the glass transition behavior, generally increased at any given wavelength with the degree of sulfonation. This was expected since the more highly sulfonated polymer possesses a larger number of electrophilic (i.e., sulfonated) rings capable of EDA complexation.

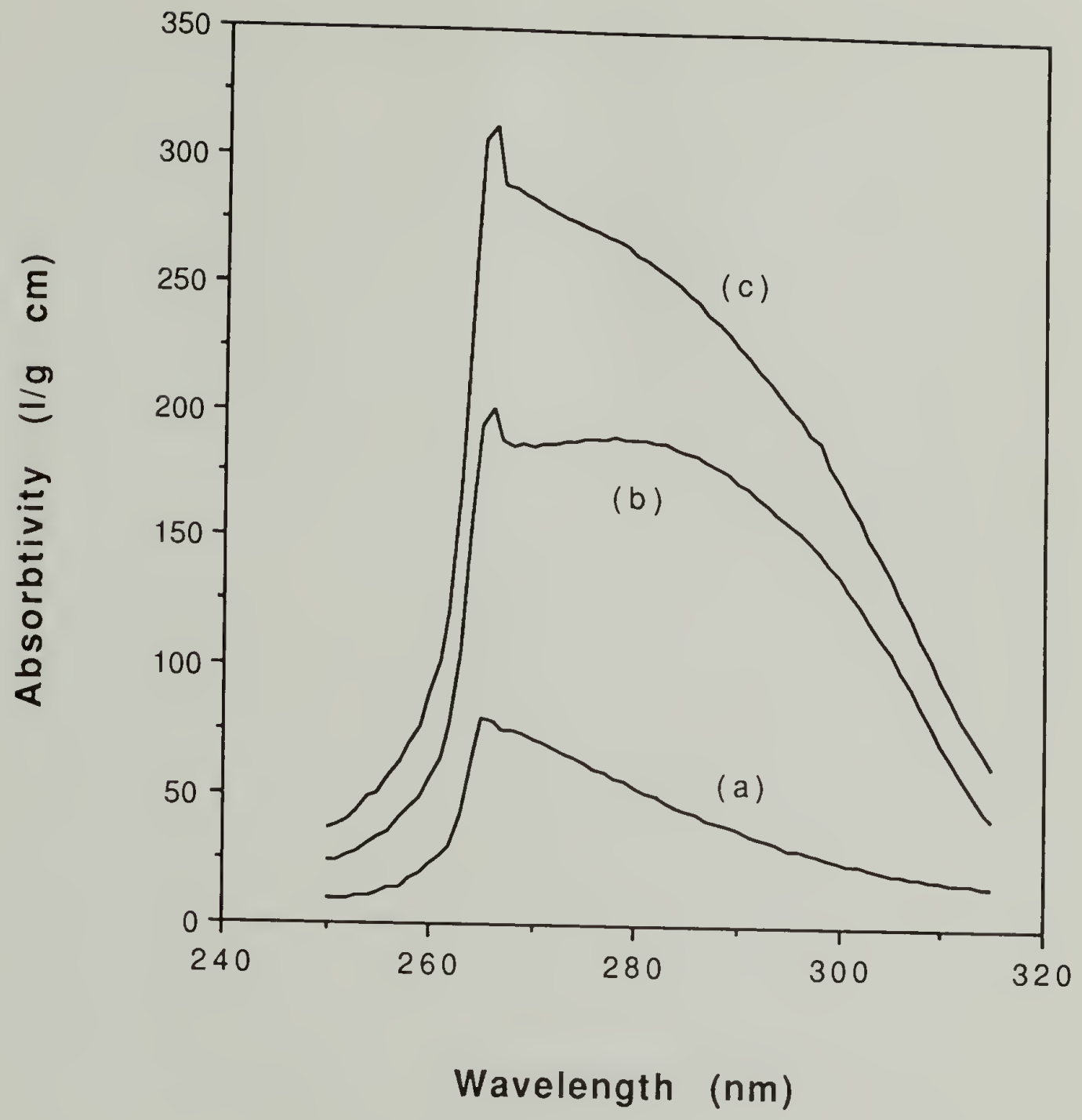

Figure 3.25. Ultraviolet spectra of PEI (a), sulfonated PEEK (b) (degree of sulfonation = 1.00) and a 50/50 (w) blend (c).

A comparison of the PAI and PEI blend spectra revealed that the degree of "excess" absorption was far greater in the PAI blends, even with the SPEEK (0.53) polymer, than in the SPEEK (1.00)-PEI system. This was expected, based on a comparison of the chemical structures of the two polyimides: for a given mass of polymer, the number of electron-donating N-phenylene moities is 3.06 times greater for the poly(amide imide) than for the poly(ether imide), allowing for participation in a far greater number of EDA complexes. A further comparison along this line was also of interest; the (normalized) number of rings capable of participating in an EDA complex (either as an acceptor or donor) was 1.00 for SPEEK (0.53) (the basis for normalization), 1.69 for SPEEK (1.00), 1.06 for PEI and 3.23 for PAI. Thus, the extent of complex formation (and hence, the degree of "excess" absorption) in the SPEEK (1.00)-PEI blend was limited by the number of available donor moities, as opposed to the number of the available acceptor moities, as seen in the PAI blends.

The positions of local absorption maxima depend principally on the ionization potential of the donor, and to a lesser extent on the nature of the acceptor. The donor moity in PEI is the m-phenylenediamine residue; this same moity, as well as the 4,4'-oxydianiline residue, acts as a donor in PAI. The maximum observed in the PEI spectra at 254 nm was in good agreement with the local maxima at 252 and 256 nm in the PAI blends (X_S = 0.53 and 1.00, respectively). Thus, this absorption peak was assigned to the m-phenylenediamine donor, leaving the other maxima

(264, 315 nm for SPEEK (0.53), 266, 315 nm for SPEEK (1.00)) to be assigned to the 4,4'-oxydianiline moity. The two phenylene rings of this latter species are chemically identical and should participate as donors in the same fashion, resulting in only one maximum. The existence, however, of two separate maxima may result from two types of EDA complexes of this moity: the case where only one of the rings acts as a donor (resulting in the lower wavelength local maximum), and the case where both rings act as donors (giving rise to the higher wavelength maximum). The existence of two maxima with only a 4,4'-oxydianiline moity present was also observed in the case of the intramolecular EDA complexation of poly(N,N'- bis(phenoxyphenyl) pyromellitimide), with the peaks occurring at 276 and 334 nm (102).

Electron donor-acceptor complexes have been observed in many polyimides of various chemical structures (102-106) and in polyimide model compounds (107-109). All of these compounds were prepared from dianhydride moities such as pyromellitic dianhydride (PMDA), one of the strongest electron acceptors known. Separation of two adjacent anhydride units along the chain by the introduction of flexible linkages

> will always reduce the strength of the CTC relative to pyromellitimide, irrespective of its electronic characteristics, because it reduces the elctron affinity of the dianhydride by isolating the powerful electron withdrawing anhydride groups from each other (110).

This was clearly seen in both PEI and PAI. The electron affinity of the anhydride moities was reduced to a degree less than the affinity of the sulfonated ring; the lowest free energy for the system was attained,

then, by the formation of intermolecular, rather than intramolecular, EDA complexes. In the case of SPEEK-PAI, this reduction in free energy was significant enough to convert an immiscible system (PEEK-PAI) to a miscible one.

Although aromatic amines are well known in the literature as electron donors, sulfonated aromatics as electron acceptors have rarely been studied. Notable exceptions to this were the formation of complexes between p-aminodiphenylamine (and its polymer) with both benzenesulfonic acid and 1-naphthalenesulfonic acid (111). The benzenesulfonic acid - polymer system was reported as having an electronic conductivity of 0.091 S/cm. (Electrical conductivity is not uncommon in EDA systems.)

3.2.3.2 Ternary

Since PAI and PEI were shown to be immiscible, yet each was found to be completely miscible with sulfonated PEEK, it was thought that SPEEK might act as a compatibilizing agent for the polyimides. The ternary phase diagrams for these blends are shown in Figures 3.26 and 3.27, for the X_S = 0.53 and 1.00 polymers, respectively. For both ternary systems there were global compositions which showed only one glass transition, indicating the compatiblizing effect of the SPEEK. For the SPEEK (0.53) system, the samples which exhibited one T_g were composed of at least 60% (w) SPEEK or at least 50% (w) PEI; none had

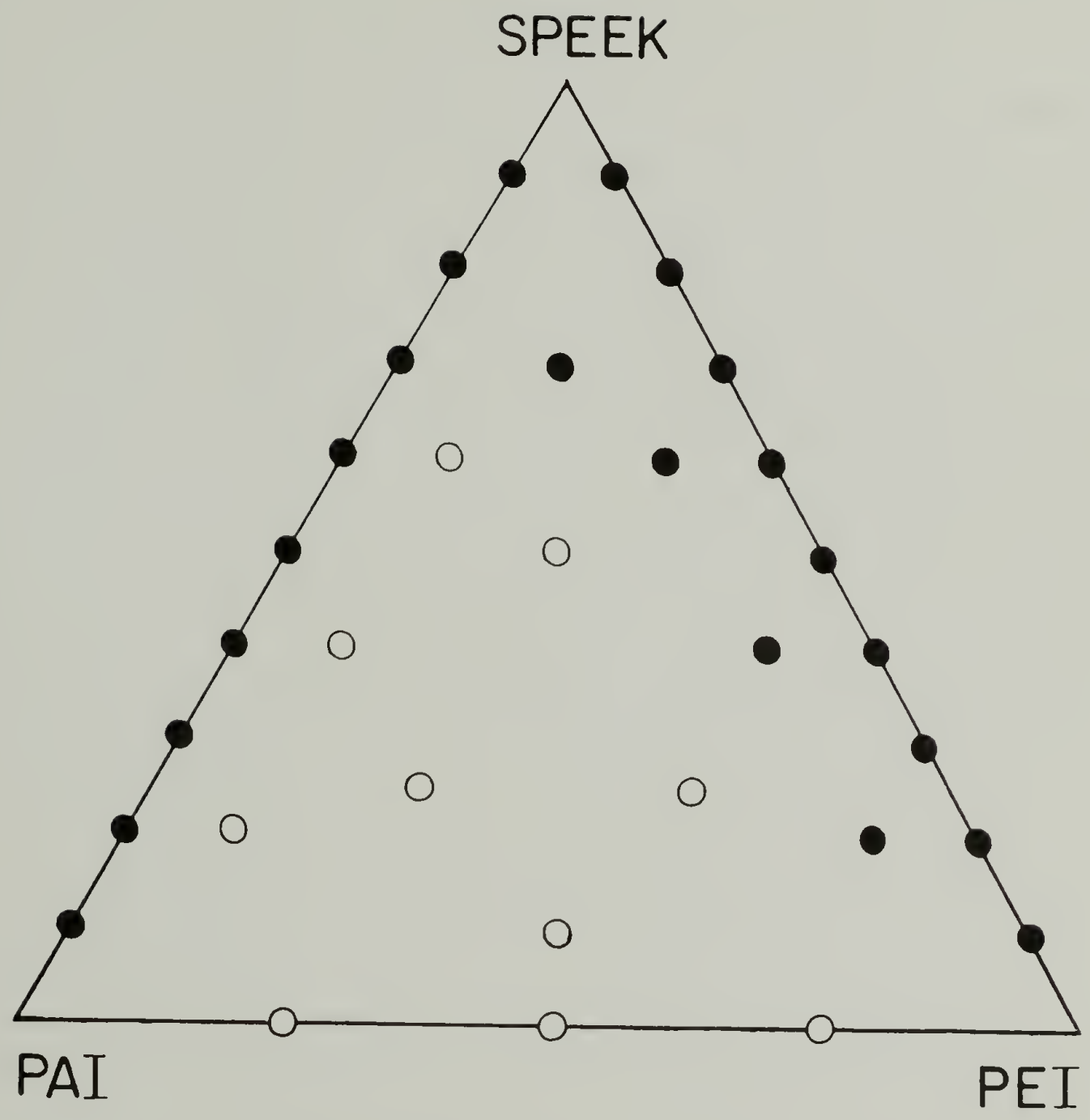

Figure 3.26. Phase diagram for the PAI-SPEEK-PEI ternary system (degree of sulfonation = 0.53). Compositions showing one glass transition (●); compositions showing two glass transitions (o).

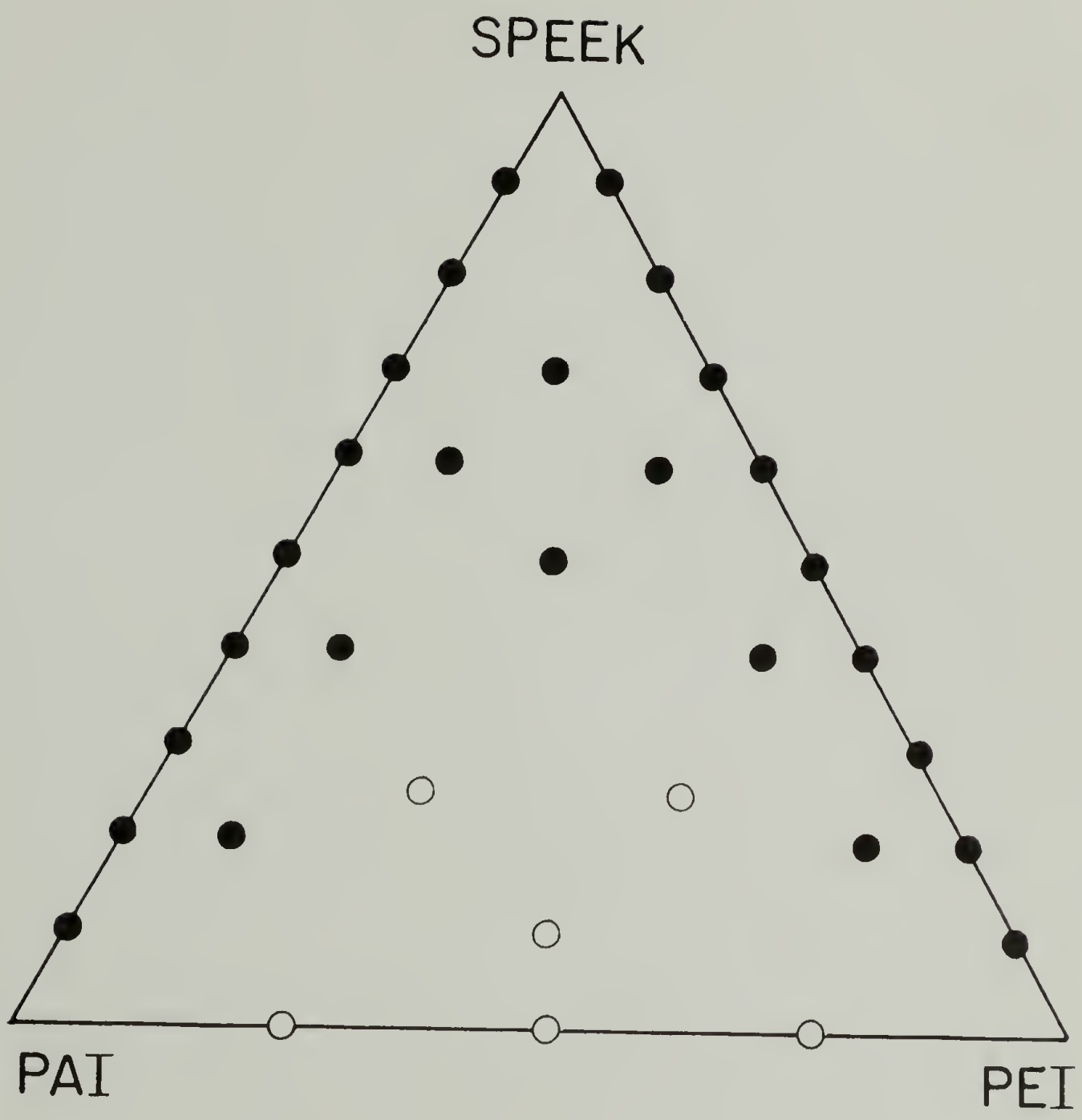

Figure 3.27. Phase diagram for the PAI-SPEEK-PEI ternary system (degree of sulfonation = 1.00). Compositions showing one glass transition (●); compositions showing two glass transitions (o).

more than 15% (w) PAI. All compositions with greater than 15% (w) PAI exhibited two separate and distinct glass transitions. This behavior was easily understood in light of the relative number of electron donor moities in the polyimides. For a given weight, PAI possesses 3.06 times as many N-phenylene rings as does PEI, and is capable of forming a larger absolute number of EDA complexes, even at a PEI/PAI weight fraction ratio as low as three. Thus, it was not unexpected that the PAI rich compositions showed two glass transitions. Also, those compositions for which the SPEEK weight fraction was less than or equal to the weight fraction of both polyimides exhibited two glass transitions.

For the SPEEK (1.00) ternary system, the region of compositions exhibiting single glass transitions increased at the expense of the two phase region, when compared to the SPEEK (0.53) system. Such a change indicated that the more highly sulfonated polymer is a better compatibilizing agent; this was expected since the SPEEK (1.00) has a greater number of electron accepting moities per unit weight (1.69 times as many) than the SPEEK (0.53). Four compositions which possessed two T_gs in the SPEEK (0.53) system were found to have only one in the SPEEK (1.00) system. Only those compositions for which the sulfonated PEEK weight fraction was less than or equal to the weight fractions of both polyimides had two glass transitions. For these compositions, it seemed that there merely was not enough SPEEK present to completely compatibilize the sample.

For both ternary systems, the majority of samples were transparent; some such samples were found to have two separate glass transitions. Thus, the condition of transparency cannot be assumed to be absolute proof of a single phase system. In the two-phase-yet-transparent samples, the indices of refraction of the phases present must be sufficiently close so that scattering was not observed by the naked eye.

For those compositions which exhibited two glass transitions, quantitative determination of the relative amounts and the compositions of each phase, based on extrapolation from the thermal behavior of the binary blends, proved fruitless. It seemed likely that the sulfonated PEEK was partitioned between both phases in the two phase compositions, since the T_g values of those phases corresponded to binary (SPEEK-polyimide) blends of intermediate composition. It also seemed possible that the separate phase in the two phase compositions might contain each of the three polymers, but with the minor polyimide (PEI in the PAI-rich phase, and vice versa) in such a small amount as for it to have no readily discernable effect on the glass transition temperature. Such minor polyimide components might be expected to be the lowest molecular weight fractions of that polymer.

3.2.4 Sulfamidated PEEK - Poly(amide imide)

Blending of a sulfamidated PEEK with a polyimide was undertaken to yield additional insight into the nature of the intermolecular

interactions leading to miscibility in the sulfonated PEEK - polyimide blends. Since no sulfonic acid proton is present in the sulfonamide, the possibilities of hydrogen bonding and acid-base interactions in the blends are eliminated. For these reasons, the careful choice of a secondary amine for synthesis was necessary, so as not to introduce any other functional groups which might interfere with or participate in specific interactions. Aliphatic amines were utilized since the hydrocarbon moities are incapable of being involved in strong interactions. Use of diethyl amine yielded a sulfamidated polymer which begin to experience degradation at approximately 220° C; the onset of degradation for the piperidine sulfonamide was determined to be 329° C, making it a candidate for blending. (Since the T_g of the piperidine sulfamidated PEEK was 215° C, blend studies with PAI only would be useful; the closeness of the SAPEEK T_g to that of PEI would render the study of that system's phase behavior impossible.)

The cast films of the SAPEEK - PAI blends were transparent and amber in color. Results of the DSC analysis of these blends are shown in Figure 3.28. For each blend sample, a single, sharp compositionally-dependent glass transition was observed, indicating miscibility. The values of the blend T_gs were all within 7-8 degrees of the values predicted by a linear compositionally-weighted average.

The phase behavior of this system independently confirmed the role of EDA complex formation as the intermolecular interaction responsible

for miscibility, yet comparison of the behavior of the sulfonated PEEK - PAI blends with that of the sulfamidated PEEK blends revealed that the very strong positive deviations in the glass transition temperatures observed in the former were absent in the latter. This difference could be understood in light of three differences (two steric and one electronic) between sulfonated and sulfamidated PEEKs. First, the size of the piperidine group of the sulfonamide is much greater than the -OH of the sulfonic acid; the presence of this bulky group most likely decreases the ability and effectiveness of electronic interaction between the sulfamidated phenylene moities and the N-phenylene rings of the poly(amide imide) by affecting relative chain positions. Secondly, each of the three phenylene rings in the PEEK repeat unit can bear the sulfonamide substituent, as compared with only one of the three rings which can be sulfonated; this broader substitution pattern (and potentially higher degree of substitution) can greatly affect the general and local chain conformation. Thus, it was possible that sulfamidated phenylenes are unable to participate in electron donor-acceptor interactions with the N-phenylene units of the polyimide due to the conformational limitations within the SAPEEK chains. Finally, although the substituted rings of both SPEEK and SAPEEK were activated for participation as electron acceptors in intermolecular complexation, the greater electrophilicity of the $-SO_3H$ moity compared to the sulfonamide group leads to the possible formation of thermodynamically stronger complexes in SPEEK compared to SAPEEK with the same electron donor.

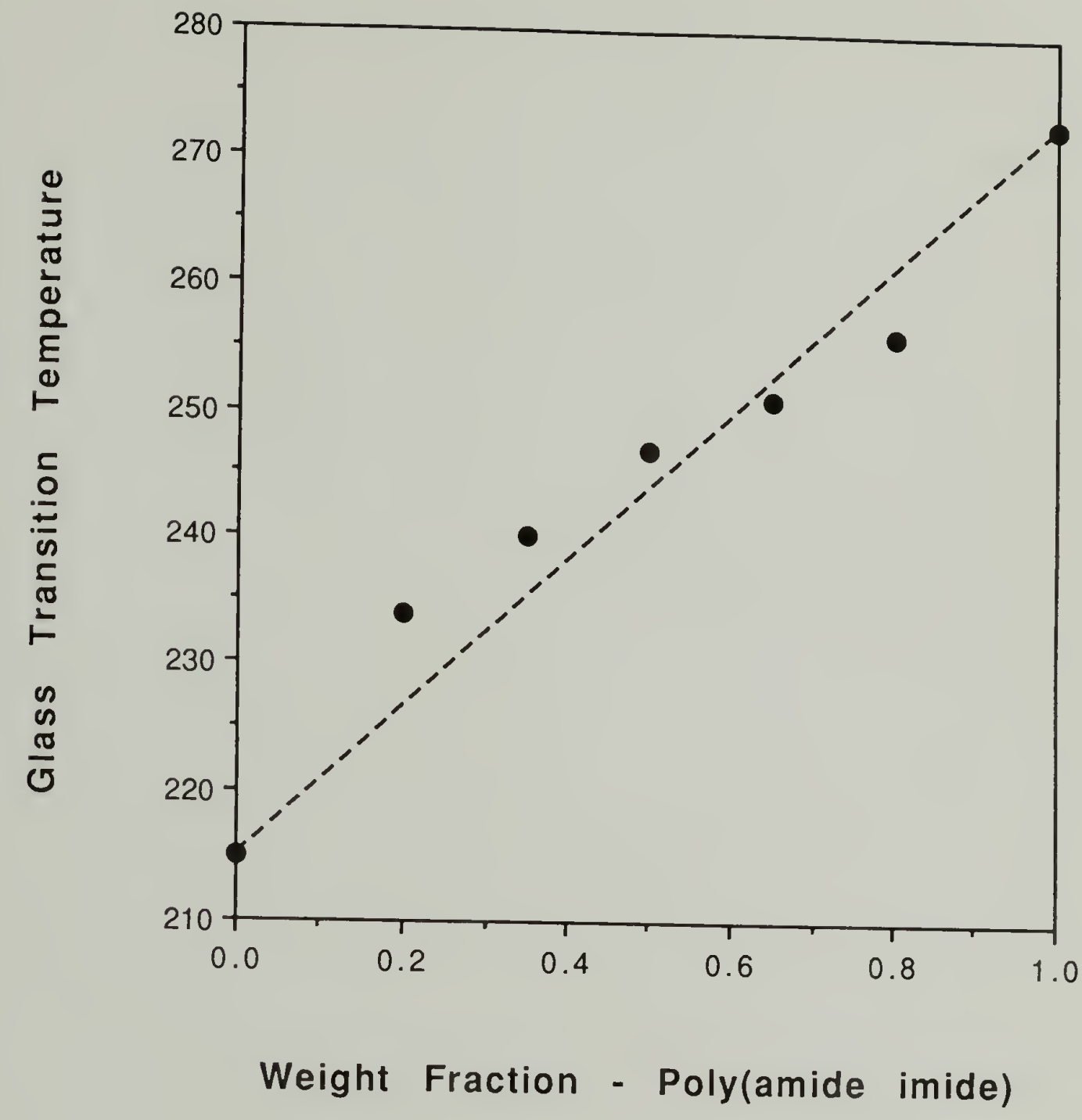

Figure 3.28. Glass transition temperatures of SAPEEK-PAI blends.

3.2.5 Nitrated PEEK - Poly(amide imide)

Cast films of the NPEEK-PAI blends were found to all be transparent, regardless of the degree of nitration. As with the PAI blends with the sulfonated and sulfamidated PEEKs, the blends were dark amber in color, with some slight variation with composition.

Results of the DSC analysis of the blends are shown in Figures 3.29, 3.30 and 3.31, for the degrees of nitration of 1.15, 2.15 and 2.79, respectively. (Due to the limited solubility of the X_N = 0.42 and 0.82 polymers, blends of these NPEEKs could not be made.) For the NPEEK (1.15)-PAI blends, two glass transitions were observed at five blend compositions; the lower T_g was approximately that of the NPEEK (1.15) homopolymer, and the higher T_g was 34-45 degrees below that of the pure PAI. The values of the higher T_gs increased consistently with higher (global) PAI content in the blends. At a sixth intermediate composition (PAI weight fraction = 0.90), only one clear glass transition was observed. The absence of a second, lower glass transition did not definitively indicate complete miscibility at this composition; it was possible that a second amorphous phase existed in such a small quantity that its T_g could not clearly be determined by DSC. In either case, the NPEEK (1.15)-PAI blends could be termed partially miscible, with one phase consisting almost entirely of nitrated PEEK and the second being rich in PAI, but containing a significant amount of NPEEK, as evidenced by the lowering of the glass transition temperature.

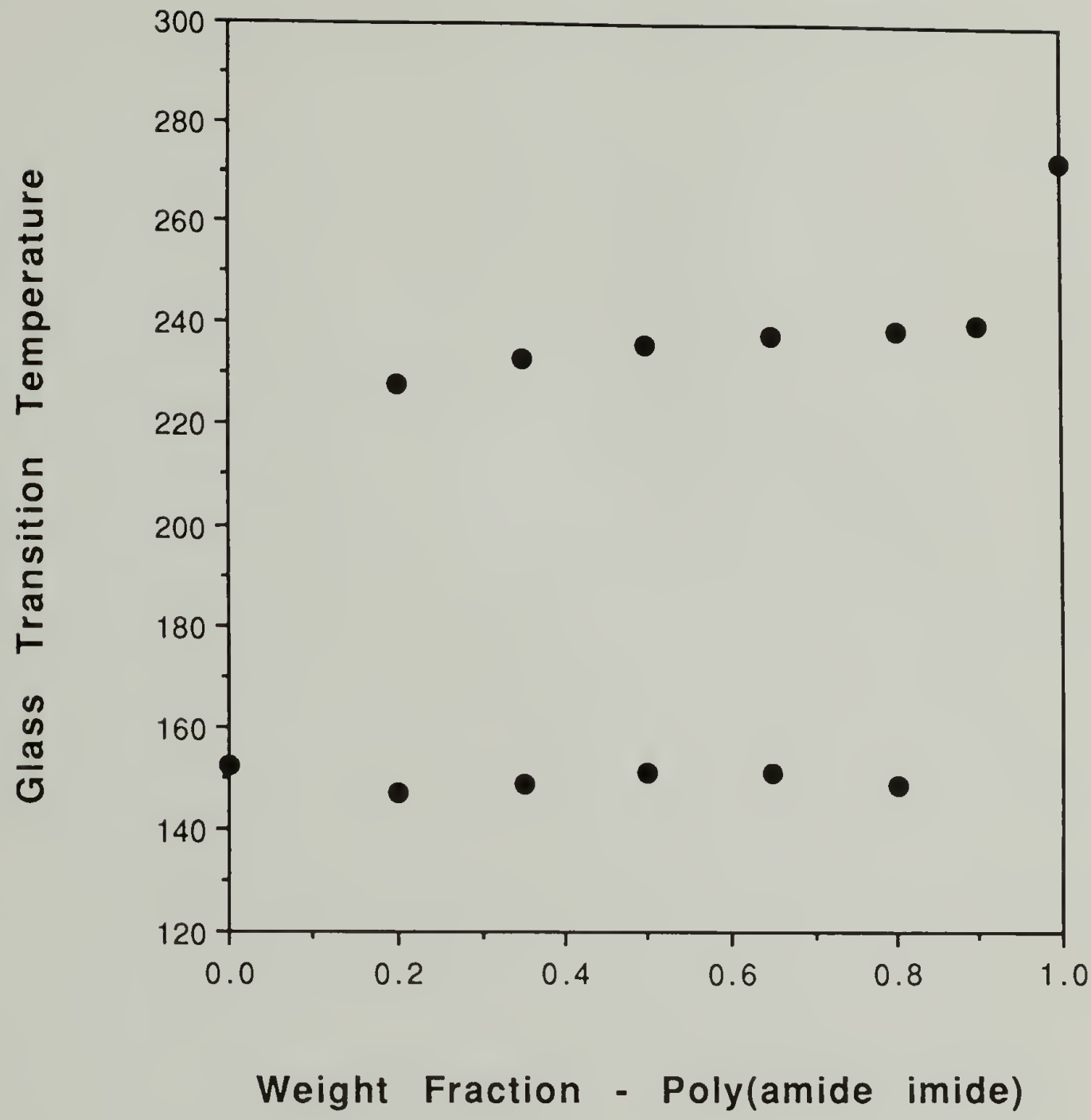

Figure 3.29. Glass transition temperatures for NPEEK-PAI blends (degree of nitration = 1.15).

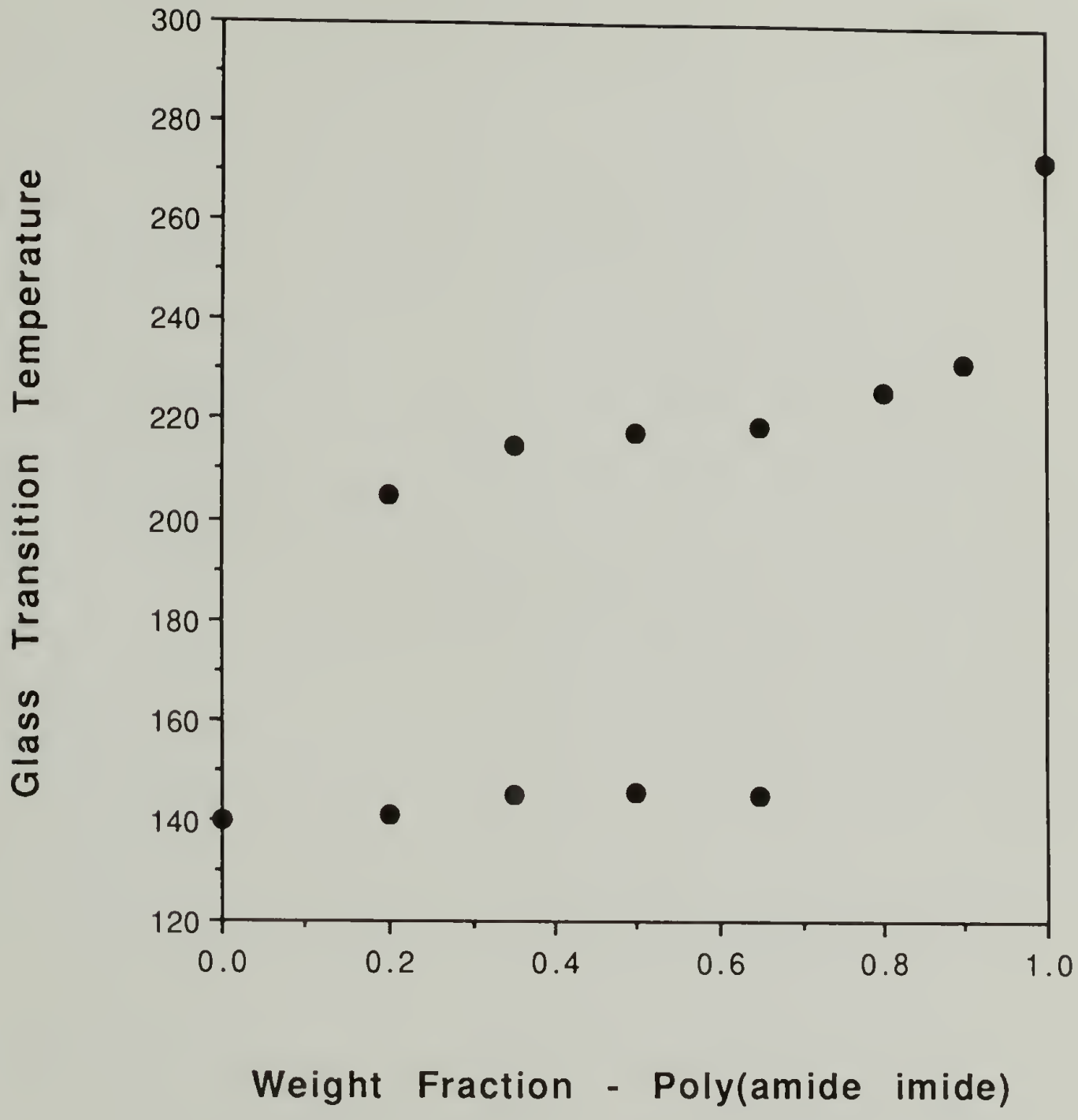

Figure 3.30. Glass transition temperatures of NPEEK-PAI blends (degree of nitration = 2.15).

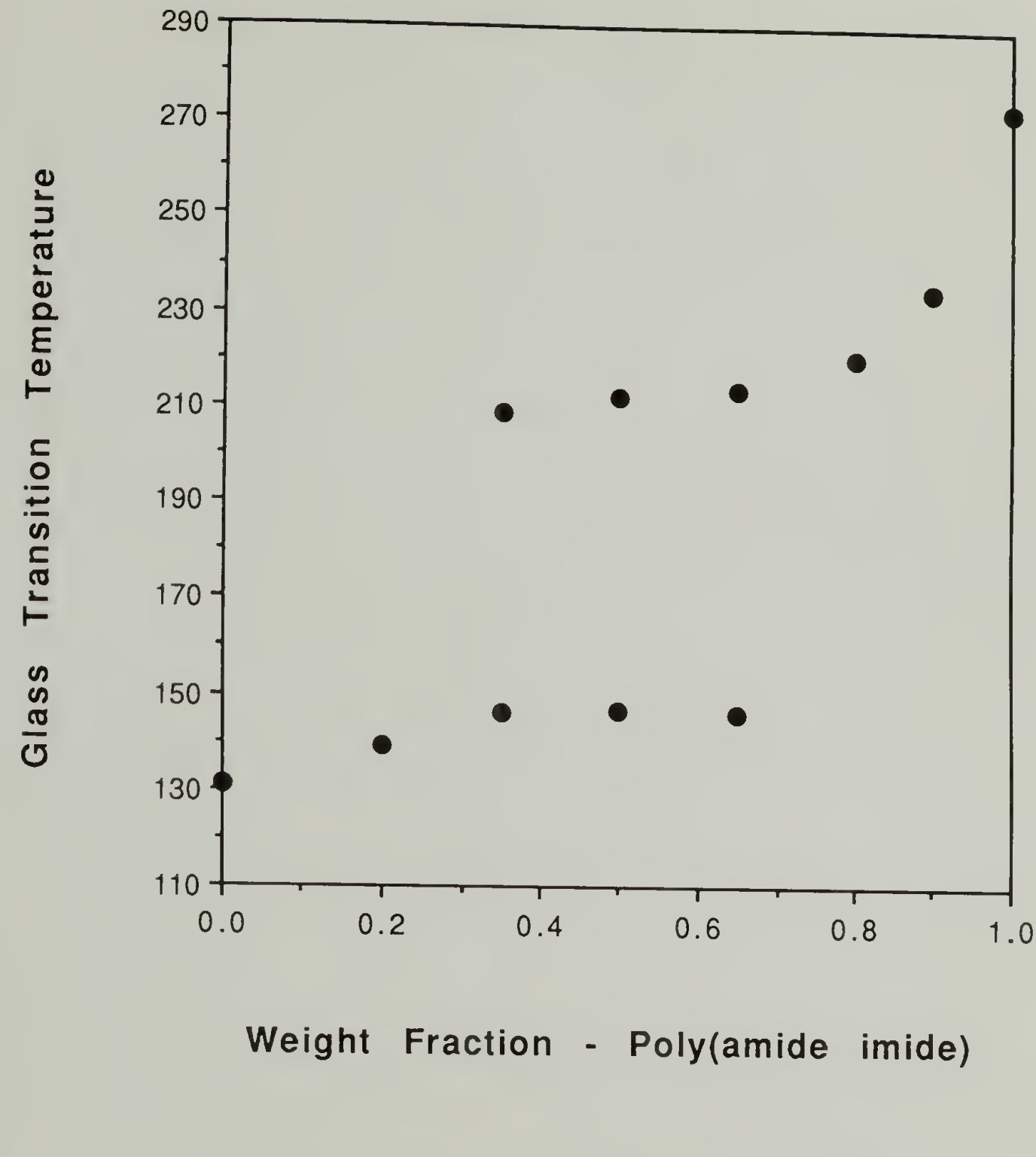

Figure 3.31. Glass transition temperatures of NPEEK-PAI blends (degree of nitration = 2.79).

For the NPEEK (2.15)-PAI blends, two glass transitions were observed for only four of the compositions examined (PAI weight fractions of 0.20, 0.35, 0.50 and 0.65). The lower T_gs for these compositions were never more than six degrees greater than that of the NPEEK homopolymer, while the higher T_gs were as much as 68 degrees below that of pure PAI. These higher T_g values consistently increased with increasing (global) polyimide content. At the two compositions with the highest PAI weight fractions, no evidence of any change was observed in the region of the lower glass transitions; only a single, distinct transition was observed for each of these compositions, with the T_g values continuing the trend of increasing with higher PAI weight fraction. Thus, the NPEEK (2.15)-PAI system could be termed partially miscible, with complete miscibility at very high polyimide content (PAI weight fraction $\geq$ 0.80).

In the NPEEK (2.79)-PAI blends, two glass transitions were observed for three compositions (polyimide weight fractions of 0.35, 0.50 and 0.65), and only one transition was observed for each of the other three compositions (PAI weight fractions of 0.20, 0.80 and 0.90). For the samples with one T_g, no evidence of any other changes were observed in either the region of the higher (PAI: 0.20) or lower glass transition (PAI: 0.80, 0.90). The lower T_g values of the blends with transitions were all 15-16 degrees above the T_g of the NPEEK (2.79) homoplymer, and the T_g of the 20% (w) PAI blend was intermediate to these. The values of the higher T_gs were as much as 64 degrees below that of pure PAI, and

again, they increased monotonically with increasing global PAI content. The compositions which exhibited only one (high) transition (PAI: 0.80, 0.90) continued in the trend of increasing T_g.

A comparison of the results from all three NPEEK blend systems is shown in Figure 3.32. In this normalized form, it was clear that the nitrated PEEK and poly(amide imide) became more miscible with increasing levels of nitration, as evidenced by the nearing of the high and low T_gs at a given composition. This increased miscibility was demonstrated also by the narrowing of the compositional window with higher nitration levels for which two glass transitions were observed. Since the average molecular weight of NPEEK was known to decrease due to ipso substitution and chain cleavage with greater nitration, the changes in phase behavior may result from either of these factors, or a combination of both.

It was surprising that the nitrated PEEKs were only partially miscible with PAI, but that other PEEKs modified to include weaker electron acceptors (sulfonated and sulfamidated PEEKs) were found to be completely miscible, especially since EDA complexes of nitroaromatics and aromatic amines are well known (112,113). The surprising phase behavior of the NPEEK blends was thought to be caused by a combination of two principally steric effects. First, a change in the general stiffness of the chain was observed in NPEEK with nitration, as demonstrated by the increase in the glass transition temperature at low levels of nitration. Certainly, this reduction in chain conformation

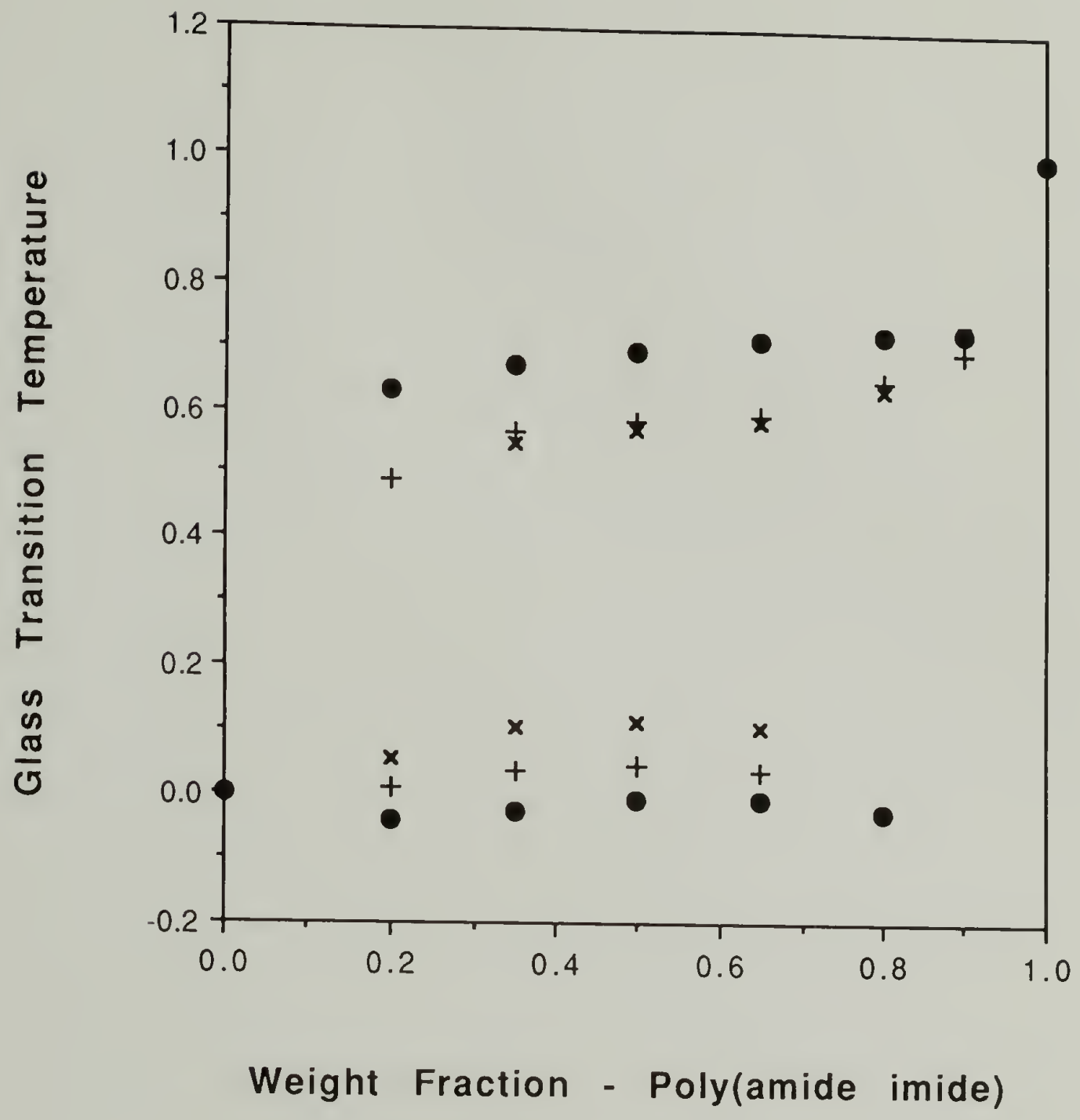

Figure 3.32. Normalized glass transition temperatures for the nitrated PEEK-PAI blends. Degrees of nitration are 1.15 (●), 2.15 (+) and 2.79 (x).

continues with higher levels of nitration, but its effect on T_g was masked by the drop in T_g caused by the decrease in the average molecular weight. Thus, a limit was placed on the number of nitrophenylene units able to participate in EDA complexes by the chain conformation.

The second factor which might also have affected phase behavior is the result of a combination of steric and electronic factors. Examination of the molecular architecture of NPEEK and PAI indicated that when a nitrophenylene acceptor and an N-phenylene donor were positioned such as they might be in an EDA complex, the oxygens of the nitro group and those of the imide carbonyls were very close, and possibly overlapped, depending on the relative positions of the two polymers. In such an event, there should be a strong electronic repulsion between these two species with enough energy to prevent the formation of a donor-acceptor complex. Also in NPEEK, since it was possible that all of the phenylene rings on the repeat unit were nitrated, the pairing of a nitrophenylene in NPEEK and an N-phenylene in PAI would strongly be affected by the existence of these electronic repulsions involving any adjacent nitrophenylene rings. Such long range effects seemed to be essentially absent in SPEEK, which at most has only one electron acceptor (sulfonated) ring per repeat unit, and very limited in the SAPEEK studied here. Thus, other factors, primarily steric in character, seemed to more significantly affect the phase behavior of the NPEEK-PAI system than did the electronic affinity of the acceptor moities. Another case were steric effects were found to

dominate EDA complex behavior over electronic factors has been systematically studied, with similar conclusions (114).

CHAPTER 4

CONCLUSIONS AND FUTURE WORK

4.1 Conclusions

This work has had two main parts: the first, material synthesis and characterization and the second, blend studies. For material synthesis and characterization, four types of polymers were prepared. Results of the controlled sulfonation of PEEK were in good agreement with previously reported data. The glass transitions of the SPEEKs were found to correlate well with the square root of the degree of sulfonation. Sulfamidation of PEEK was first performed, based on previous work on other poly(aryl ether ketone)s. The rate of PEEK sulfamidation was found to be greater than that of PEKK, resulting from the difference in the electronic character of the two polymers.

The first reported nitration of PEEK was performed; five degrees of polymer nitration were achieved. Infrared spectroscopy and carbon-13 NMR results demonstrated that each of the three phenylene rings in the polymer repeat could be nitrated, according to the availability of the reagents. Lower degrees of nitration resulted in increased glass transition temperature, while higher degrees of nitration ($X_N > 1$) resulted in relative decreases in T_g. This was explained by the occurrence of a two-step nitration process: initial substitution

occurring at the oxy-1,4-phenyleneoxy ring, and later reaction occurring on phenylene rings adjacent to the carbonyl, with some ipso-substitution taking place. This latter type of substitution led to chain cleavage, and was confirmed by carbon-13 NMR and by solution viscosities. Nitrated PEEK was found to be significantly less thermally stable than PEEK, but was also significantly more soluble, primarily in polar, aprotic, electron-rich solvents.

Reduction of the nitro groups of NPEEK to amino groups was achieved using zinc and acetic acid. The reduction was confirmed by infrared spectroscopy, but was found to be less than complete. Aminated PEEK was found to have slight differences in thermal stability and solubility from its parent nitrated PEEK.

Several important results were found regarding blends of polyimides, PEEK and chemical derivatives of PEEK. The immiscibility of the binary PEEK-PAI and the PEI-PAI systems was determined. (Blends of PEEK with PEI were previously reported in the literature as being completely miscible.) Chemically modified PEEKs were found to have greatly different phase behavior with polyimides when compared with unmodified PEEK. Thus, three new binary blends, miscible at all compositions were discovered: sulfonated PEEK - poly(ether imide), sulfonated PEEK - poly(amide imide) and sulfamidated PEEK - poly(amide imide). Ternary blends of sulfonated PEEK and the two polyimides were also studied with the SPEEK acting as a compatibilizing agent to induce miscibility at

some compositions. The sulfonated PEEK blends showed strong positive deviations in the glass transition behavior, suggesting the presence of strong intermolecular interactions. Infrared studies of SPEEK-PAI blends yielded no conclusive evidence for the occurrence of either hydrogen bonding or an acid-base interaction in the blends. Deviations from Beer's law absorption behavior in the ultraviolet spectra of the sulfonated PEEK blends were observed. Nitrated PEEK was found to be partially miscible with PAI at three different degrees of nitration.

The miscibility and phase behavior of the substituted PEEKs with the polyimides were postulated to result from the formation of an intermolecular electron donor-acceptor complex between the substituted phenylene ring in the PEEKs and the N-phenylene units of the polyimides. Confirmation of the formation of such complexes was demonstrated by the anomalous UV absorptions for the sulfonated PEEK blends, and by the miscibility of the sulfamidated PEEK with the poly(amide imide). The strength of the electron donor-acceptor interactions, and thus the phase behavior of the blends, was found to be tempered by steric factors depending on the exact nature of the electrophilic substituents and the general and local conformation of the polymer chain.

4.2 Suggestions for Future Work

Several areas of further research can be derived from this study. As with this work, some of these areas principally involve material

synthesis and characterization and some involve blends and electron donor-acceptor interactions.

In the reduction of nitrated PEEK to the corresponding amine, three methods were attempted, with only one being effective. Other methods, such as catalytic hydrogenation, could be tried to produce APEEK.

In this study, sulfamidated PEEK was prepared using a mono-functional amine. Use of diamines would lead to the formation of an interesting network, which would be expected to retain the high glass transition and thermal stability of PEEK.

As many EDA complexes are known to be conductive, futher study of this aspect is warranted. Specifically, nitrated PEEK might be able to be doped with a small molecule donor to form a conductive system.

Finally, adaptation of the knowledge gained regarding EDA complexes in the work could by made be chemically modifying the surface of PEEK fibers for use in polyimide-matrix composites. Such treatment could be expected to result in strong fiber-matrix adhesion.

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